Karoliine Bürkland

PLASTIC: FAR FROM FOREVER

Understanding the Degradation, Preservation, and Conservation of Plastic Objects

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EESTI RAHVA
MUUSEUM
Estonian National Museum

ICOM international council of museums Estonia

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Plastic: Far from Forever
Understanding the Degradation, Preservation, and Conservation of Plastic Objects
Edited by Karoliine Bürkland
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Foreword

This book was written six years ago – a fleeting instant in the big picture, but for a practising conservator, ample time to revisit the efficacy of various conservation methods and to become better at one's craft. Reading through the instructions and explanations I wrote in 2019, I realised it was necessary to update a few points.

In the first chapter, devoted to the fundamental nature of plastics, I tried to elaborate a little and convey the subject matter so it could be more easily grasped. I revisited the plastics covered in Chapter 2 and added a few observations on characteristics of their ageing and preservation that are important from a conservator's perspective. Chapter 3, "Identifying Plastics", received more extensive additional passages. In the interim period, I had taught a number of workshops for university students and already practising conservators. Each time, some intriguing question or perspective comes up and I myself learn something new from every workshop.

The sections on ageing of plastic received a handful of changes, but not as voluminous as in the last chapter of the book, which introduces methods for conservation of plastic. For example, I turned the system for evaluating the state of plastic museum items upside-down, because in practice it works better in inverted form.

Naturally, I could have easily written many additional chapters for this book. It's still missing an entry on a biodegradable plastic, polylactic acid (PLA), which thanks to EU directives has replaced Styrofoam in disposable utensils and tableware production lines. It is also used as filament for ever more popular 3D printers. Indeed, other biodegradable plastics ought to be described as well, since that is the direction in which plastics are slowly but inexorably heading. Biodegradable plastics will one day be found in museums, symbolising a new era in plastics – and these materials are far from forever." But it seems to me that they merit a separate book of their own…

Karoliine Bürkland
Spring 2025

Introduction

It was the late 1990s. I had just received a very cool toy – a rainbow-coloured Slinky with a star-shaped cross section (the coil that can “walk” down stairs). Although it kept on getting tangled up and I spent most of the time untwisting its coils, I still got a lot of fun out of it. One late afternoon, my teenage brother offered to show me a trick with the Slinky. I was transfixed. From behind his back he produced a half-litre glass bottle. He forced the Slinky coils around the bottle, and then placed the assembly in the large pot of hot water that was always simmering on our stovetop. A moment later, he deposited it in a bucket of cold water, which was also near the stove. With a triumphant “Ta-da!”, he handed me back my Slinky, now a lopsided cylinder. “Now you have a spring with a different shape!” Well, I can tell you that his audience was not at all satisfied with this “magical” transformation.

Many years later, thinking about thermoplastics, I recalled the episode with the Slinky. It was the first time I had experienced their main characteristic – their ability to be re-shaped by heating. But what else can be done with plastics? Well, just about anything!

Excellent electrical, sound and thermal insulating properties; the ability to withstand weather conditions, high or low temperatures and physical stress; impact resistant; lightweight; the ability to be shaped into an unlimited range of forms – these are just some of the qualities that make plastic the preferred choice of material for manufacturers. Plastics are among the most multifaceted materials in the world. The same polymer can be turned into materials with a wide array of attributes. For example, polyurethane can be used to make durable construction elements, elastic fabric, faux leather, solid or soft foam and even adhesives and varnishes. If the characteristics of a certain plastic need to be modified – for example, to make it more tolerant of low temperatures – this can be done with additives. If plastic needs to be more resistant to impact, other polymers can be added to it to form co-polymers. Much hinges on the manufacturing method, too. Polyethylene terephthalate (PET), used to make soft drink bottles, softens at 80 °C. The plastic bags that lock in moisture for roasting are also made of polyethylene terephthalate. But why don’t they melt and ruin the chicken inside? It’s because the plastic in the cooking bag was stretched in two directions during the manufacturing process, which changed the molecular structure of the polymer. Yes, the world of polymers is confusing but fascinating!

Since we live in a time when plastic objects are so commonplace that we barely even notice them, the amount of plastics in museum collections may be surprising. The first objects were mainly artworks. As early as the 1920s, sculptors discovered that plastic allowed them to realise their artistic vision in novel ways. The largest acquisitions started in the 1970s, when plastic objects had become symbols of technological progress, design and pop culture. By the 1980s, the colourful bracelets and earrings of the 1960s had taken on vintage status, and as such were sought after by both museums and collectors. And as mentioned earlier, the possible uses of plastics are endless, so plastic can be found in furniture, applied art, textiles, technology and art items.

In the 1980s, an alarming phenomenon began to be observed in museums' plastic object collections. Some became sticky or brittle or crumbled into pieces. In the early 1990s, the Victoria & Albert Museum in London conducted the first thorough investigation into the status of its plastic objects. This is now considered to be the beginning of plastic conservation. It was the first time that attention began to be devoted to the degradation of plastics. The first conferences were established to raise awareness of the matter. By the middle of the decade, preservation conditions and methods meant specifically for plastic museum pieces were devised. Our store of knowledge about degradation and preservation of plastics is a far cry from our mastery of caring for ceramics, oil paint or natural textiles. Humans have been making plastics industrially for only 150 years, give or take (nitrocellulose production began in the 1860s). On the other hand, ceramics date back 6,000 years, cotton was cultivated 4,000 years ago and the peak era for oil paint was in the 16th century. It is through trial and error that materials are perfected, and so, too, the techniques for maintaining them. It takes time to evaluate which decisions are good and bad. A century and a half seems a laughably short time compared to millennia. Yet the number of plastics in use during this time has reached the hundreds. Most of them have their own little flaws that make it doubtful that they can last for centuries. Many plastic items acquired by museums weren't meant to last forever, anyway. Although the first advertising slogan for plastics was related to their durability – for example, melamine tableware was recommended for replacing ceramics because it doesn't break – manufacturers realised soon enough that plastic was a great material for cheap mass production. If modern consumers plan on using a plastic item only once or for a short period, why should a manufacturer make it last 100 years? So the work of a plastic conservator is an upstream battle right from the beginning – our job is to preserve the unpreservable, armed with knowledge that dates back only a few decades. Yet action is urgently required, because otherwise Estonian applied art classics such as the Vana Toomas table lamp, Kommunaar shoes, Salvo skis and Polümeer's caterpillar toys may disappear in a few more decades.

Hopefully this book will help in ensuring that the plastic objects that have become part of our culture can last a few more decades. I made a point to introduce the most commonly used plastics in everyday life to illustrate how versatile these materials are. A separate chapter provides a guide for how to differentiate plastics. The importance of this skill becomes evident in regard to decay, as many plastics degrade for different reasons. Even more critical (and fascinating) is the fact some plastics harm other materials as they age. To protect plastics against degradation, it's important to know what can potentially damage them and how they age. For example, sunlight is one of the main enemies; merely moving an object to a shadier place will extend its lifespan.

The chapters on preservation and conservation give an overview of methods developed in different places in the last few decades – the result of six years of research during which I combed through articles, books and scientific papers, attended a plastics course in Amsterdam and heard from different countries at a specialist conference in Munich. I tested the identification and conservation methods I described and found the results to be satisfactory. Yet it can't be claimed that these are necessarily the best techniques.

They're simply the best we have so far. It is possible that in a year or two, new conservation methods will have been developed. After all, this is still an emerging branch of conservation science.

So don't take the guidance in this book as set in stone. It's more of a manual that contributes to the promotion of plastic conservation and makes a useful addition to a conservator's bookshelf, a handy guide for looking up the characteristics of a specific plastic or to double-check a conservation technique. Hopefully it will also be accessible in the libraries of schools that teach conservation, allowing students to familiarise themselves with the essence of plastic and how it can be preserved. It might also enrich the knowledge of collectors, helping them distinguish genuine materials from imitations. It should also broaden the horizons of everyone who is interested in the history and development of plastics.

1.

WHAT IS A PLASTIC?

Plastics[1] (from the Greek πλαστικός (*plastikos*), “mouldable”) are organic compounds that can be moulded under certain temperature and pressure conditions. They may be of natural or synthetic origin. Amber, horn, bone, leather, tortoiseshell and bitumen were shaped by craftsmen back at the height of Ancient Egypt and Babylon’s power. Some natural polymers can be processed chemically to improve properties and make them easier to work. These are called semi-synthetic plastics, and examples include vulcanised natural rubber and casein formaldehyde (made from milk protein). A third category is synthetic plastics, which began to be produced in the first decade of the 20th century. The oldest of the latter is phenol formaldehyde – often known as Bakelite[2].

The word “polymer” also comes from the Greek – πολυμερές (polumeres), meaning “many parts”. As a chemical term, the word was first used by the Swedish chemist Jöns Jacob Berzelius in 1833[3] to refer to substances with the same chemical formula with different physical properties. Today’s understanding of polymers is from the 1920s, when German chemist Hermann Staudinger had the idea that polymers were composed of smaller repeating parts called monomers that became bonded into very long macromolecules as a result of a polymerisation reaction.

Synthetic monomers are obtained mainly from processing natural gas and petroleum. Benzene extracted from crude oil is used to make styrene and phenol monomers, while xylene is turned into phthalic acid, and used to synthesise polyethylene terephthalate (PET). Ammonia from the reaction of nitrogen and hydrogen is used to produce urea, melamine and acrylonitrile.[4]

The monomers in the macromolecules occur in a specific sequence, forming very long chains with a specific structure. Based on the shape of the chain, polymers are classified as either linear, branched or cross-linked polymers (Figure 1).

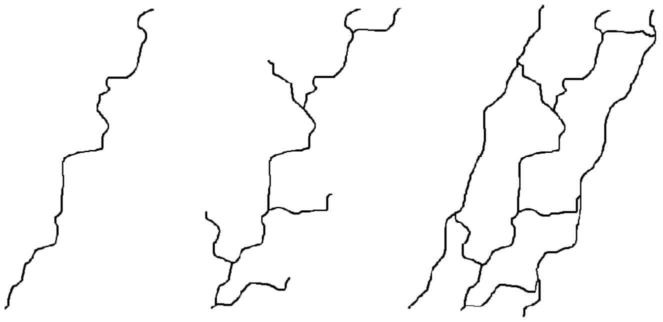

Figure 1. A – linear chain; B – branched chain; C – cross-linked chain.

The resistance of plastic to temperature, chemicals and mechanical abrasion is related to the shape of its polymer chain. Polymers with a linear or branching chain are elastic at room temperature and easily soluble in organic solvents. When heated, they develop plastic properties, and harden upon cooling. The heating and cooling cycles can be repeated many times without significant decline in the material’s properties. Such polymers are called thermoplastics. Cross-linked chain polymers with a three-dimensional latticework, on the other hand, cannot be reshaped by heating. Once the material has hardened, it cannot be softened and moulded. These are hard and brittle materials that generally expand in organic solvents but do not dissolve. Such polymers are called thermosetting polymers or thermosets.[5]

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[1] The words “plastic” and “polymer” should be distinguished to prevent later confusion: the first is a material and the second is a macromolecule.

[2] Mossman 2008: 35.

[3] Christjanson 2008: 17.

[4] Christjanson 2008: 29.

[5] Mauring 1985: 7.

1.1. Crystallinity

Depending on their shape, the polymer molecule chains can be tightly packed, forming regular crystalline structures (crystalline polymers) or be arranged irregularly, akin to a plate full of spaghetti (amorphous polymers). The less branching there is in the molecular chain, the easier it can be compressed. For instance, polyethylene, which has a linear chain, readily forms a crystalline structure (Figure 2), while it is very hard for polystyrene, with its branching phenyl (aromatic ring) groups, to do so.

… – CH2 – CH2 – CH2 – CH2 – CH2 – CH2 – CH2 – CH2 – …

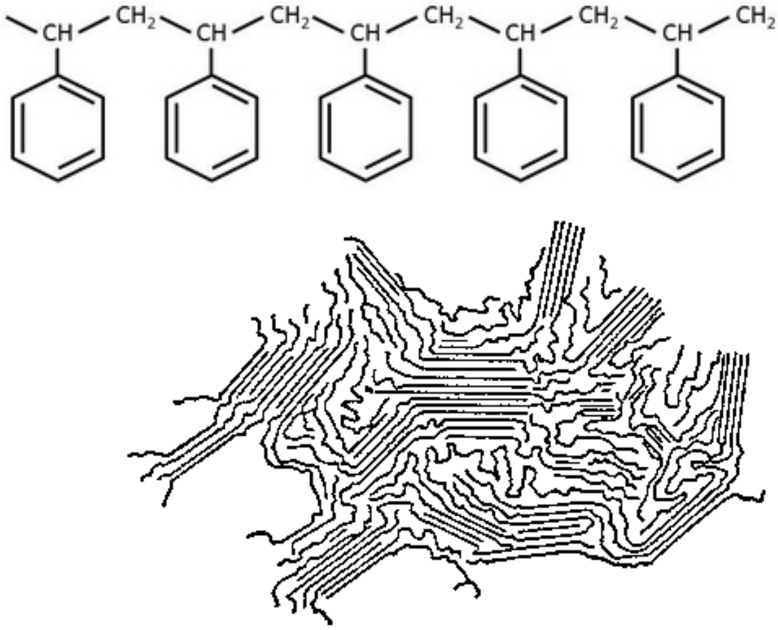

Figure 2. Top: a polyethylene molecular chain. Middle: a polystyrene molecular chain. Bottom: compressed crystalline polymer chains alternating with amorphous areas.

To a degree, all polymers are crystalline, but a completely crystalline polymer is an impossibility. The higher the degree of crystallinity, the denser the polymer's molecular structure and the more opaque the resulting plastic is. This is because in a crystalline polymer structure, tightly packed molecular chains in ordered regions alternate with amorphous areas (Figure 2). As a result, the structure of the crystalline polymer varies. Light absorbed by the material passes through certain areas but refracts upon encountering more dense crystalline areas.[6]

Examples of cloudy plastics with high crystallinity are polyethylene,[7] polypropylene and Teflon. On the other hand, amorphous polymers, such as polyethylene terephthalate and polystyrene, are ideally transparent. Plastics made of crystalline polymers usually have greater rigidity, superior mechanical characteristics, lower solubility, and a higher melting point.[8]

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[6] Painter, Coleman 2009: 25.

[7] HDPE is significantly more crystalline than LDPE, which is used to produce transparent film. HDPE has a higher level of crystallinity than LDPE, as its polymer chain branches less and is thus more compact.

[8] Lippmaa 2001: 75–76.

1.2. Glass transition temperature

Amorphous polymers may occur in two aggregate states. Some plastics (such as polymethyl methacrylate) are rigid and fragile at room temperature. Yet others (like natural rubber) are elastic in the same conditions. If the first kind of plastic is heated to a high enough temperature, a softening occurs. If the second type of plastic is cooled down enough, on the other hand, it loses its elasticity. Although the range can be quite wide (10–40 °C), a single temperature where the transition takes place is usually specified, and this is called the glass transition temperature (Tg).

The glass transition temperature range depends on several factors, one of which is the strength of the intermolecular bonds. The greater the strength of the bonds between the molecules, the more thermal energy it takes to mobilise the polymer chains. The strength of the bonds between molecules can be influenced by adding plasticisers. The plasticiser molecules insert themselves between the polymer chains, thus allowing the chains to move more freely (like a sauce on spaghetti). In this way, the softened plastic becomes flexible at a lower temperature. To a great degree, Tg also depends on the length and structure of the molecular chains.[9]

1.3. Composition of plastics

To turn a polymer into suitable plastic, additives are used such as hardeners, fillers, plasticisers, stabilisers, dyes and sometimes even other polymers.

Hardeners give plastic rigidity and mechanical strength. Acid anhydrides and sulphur (used for the vulcanisation of rubber) can act as hardeners. Hardening reactions cause cross-linking of the molecular chains in linear or branching polymers.[10]

Plasticisers make plastic more elastic and cold-resistant. Plasticisers include organic substances with a low molecular weight, chlorinated paraffins and certain oils.[11] The best-known plasticisers are the phthalates. These are chemicals of manmade origin used for example in PVC and cellulose acetates.

Fillers are added to plastic to increase mechanical strength, as a flame retardant, or to conserve the amount of polymer used. These are solid compounds that do not react with the other components in the plastic. Distinctions are made between powdered, granular and fibrous fillers. Powdered or granular fillers are sand, talc, chalk, graphite, carbon, cement, aluminium oxide; fibrous fillers are asbestos and glass. Cellulosic fillers are wood dust, textile waste and paper.[12] Gaseous fillers (like carbon dioxide, nitrogen and oxygen) are used for plastic foams.[13]

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[9] Rosen 1993: 107–109.
[10] Mauring 1985: 9.
[11] Quye, Williamson 1999: 28.
[12] Mauring 1985: 17.
[13] Shashoua 2008: 67.

Stabilisers help keep plastic's properties constant during processing and use. Their function is to prevent chemical reactions between oxygen, heat and light. Amines, phenols, metal compounds and carbon can be used as stabilisers.[14] Over time, the stabilisers are used up, and at that point, plastic begins ageing faster. As to when the added stabilisers enter this senescent phase, that can be hard to determine. It is influenced by the conditions in which the item is used and stored.

Dyes and pigments are added to plastics to impart colour. Dyes are organic chemicals that dissolve in a polymer. Pigments, which may be organic or inorganic, do not dissolve in polymers. Some mineral pigments (such as zinc oxide) can function both as fillers and as pigments. The pigments most frequently used are titanium oxide, metal powders, cadmium sulphide, zinc oxide, ultramarine, carbon and iron oxides.[15]

Lubricants improve the properties of plastics in the molten state, enabling better processability. Their goal is to migrate to the surface of the form. The resulting thin layer on the surface of the form reduces adhesion. The lubricants used most often are stearic acid and paraffin wax.[16]

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[14] Mauring 1985: 17.
[15] Quye, Williamson 1999: 28.
[16] Shashoua 2008: 67.

2.

THE MOST COMMON CONSUMER PLASTICS

Millennia ago, humans were already inventive and able to make good use of the materials found in nature. Horn, hoof, tortoiseshell, bitumen, rubber sap, shellac and amber are natural plastics that were used in their raw form. Not until the 1820s did plastic material processing technology start seeing noteworthy advances. The Industrial Revolution was under way and brought new machinery and new possibilities. The advent of oceanic steamship routes in the 1840s gave plastic development a major boost, opening the door to exotic raw materials like natural rubber from across the globe. The laying of the telegraph cable across the Atlantic and the first communications sent on 16 August 1858 were just as noteworthy, even being called the eighth wonder of the world. Previously it could take 10 days or longer for messages to be sent from Europe to America, this being the duration of a sea voyage. How wonderful to be able to send and receive information between continents – one character of text every two minutes! The world's first transatlantic telegraph message was 99 words long and was sent from Queen Victoria to US President James Buchanan in Washington. It took 17 hours and 40 minutes.[17] The excitement fizzled less than a month later when the cable, which had taken four years to lay, was burned out by excess voltage. The replacement cable, however, transmitted its first message at a speed of eight words per minute on 28 July 1866, and that was the true dawn of the Information Age.[18]

There were many reasons for adopting the use of plastics. First of all, luxury materials such as ivory, tortoiseshell and silk were already in short supply by the 19th century. The same was true of everyday commodities such as natural rubber, which had to be imported from faraway lands. The first to find a good substitute for rubber was in fact based in Estonia – a Tartu University pharmacy professor (1895–1918) originally from Russia, chemist Ivan Kondakov. In 1900, he published a method for synthesising dimethylbutadiene, which could be used to make methyl rubber, the very first synthetic rubber.[19, 20] Kondakov's methods were refined in German labs, but the German forces during the First World War were unable to benefit from the rubber substitute, because trading routes had been blocked and made it unobtainable.[21]

Another reason for the search for synthetic polymers was the fact that natural materials were unstable. For example, in raw form, natural rubber becomes brittle in cold conditions and soft and sticky when it is warm, and wood also shrinks and swells as relative humidity changes, causing it to warp and crack over time. Moreover, the refining of natural materials was slow and complicated, requiring specialist skills. Increasingly, the price of the end product reflected these limitations.

The following chapter gives an overview of the most common types of plastic in museum collections. A compact table is provided for each plastic[22], listing basic parameters such as when it was first introduced, its properties, degradation and preservation.

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[17] Famous Messages …

[18] Cogan 1985: 1–15.

[19] Loog, Timotheus, Järv 2012: 19.

[20] Past, Ilomets, Tankler 2009: 39–42.

[21] Gliech 2015.

[22] The information in the tables comes from the following sources: POPART Damage Atlas; Christjanson 2001; Christjanson 2007; Christjanson 2008; Christjanson 2010; Birley 1988; Brydson 1999; Horie 2006; Horie 2010; Loog 2012; Mauring 1985; Rosen 1993; Shashoua 2008; Rubin 1990; Whelan 1994; MODIP Identification Route Map Professional Plastics. Physical Properties of Plastics; Luxford 2007; Omnexus, Glass Transition Temperature; Matbase; Ellis, Bryan; Smith, Ray 2008; Reboul, Bakelite; Plastiquarian, Timeline; Horie 2010 [1987]; Rivers, Umney 2003; Negoita, Cristache, Bodor 2016.

The table is followed by a brief introduction to the history and description of the various products made from the material.

2.1. Semi-synthetic plastics

2.1.1. Natural rubber

Abbreviation	NR
Category	Thermoset
Discovered by	1823 – Charles Macintosh, Scotland (solubility in petrol) 1844 – Thomas Hancock, England; Charles Goodyear, USA (sulphur vulcanisation)
Derived from	Latex from rubber trees (first and foremost *Hevea brasiliensis*), *cis*-1,4-polyisoprene.
Production	Industrial production started in the 1840s. In the 1940s, its popularity waned due to synthetic rubbers being introduced.
Examples of product names	Vulcanite, Ebonite, hard rubber.
Production methods	Pressing, calendering.
Solvents	Chlorinated hydrocarbons, fuels and oils.
Glass transition temperature	Tg = –70 ˚C
Usage temperature	−50–85 °C
Rigidity	The more sulphur and fillers are added, the more rigid the material becomes.
Density	$\rho = 0.93\ g/cm^3$
Colour	Black, dark brown, reddish and other colour tones (depends on the filler).
Odour	Sulphurous, like rubber boots.
Usage	Vulcanite has been used to produce small household objects (smoking pipes, combs, jewellery, pens) while soft rubber has been used for Wellington boots, hoses, toys, inflatables, foam rubber mattresses, upholstery.
Pros	• Withstands abrasion and tearing well. • Retains elasticity at a low temperature.
Cons	• Natural origin (depends on tree growth and plantation managers). • Sensitive to oxygen, oxidizes quite rapidly. • Poor at withstanding higher temperatures and sunlight. • Vulnerable to many solvents. • Is unstable in regard to temperature change if not vulcanised (brittle in cold, sticky in heat).
Ageing	• Oxidation – crackles, shrinks and becomes brittle. • Hollow items may become sticky and appear melted. • Hydrolysis – gives off sulphur compounds (sulphuric acid). • Causes corrosion of metals it comes into contact with. • **Malignant plastic!** (harmful to other items in museum collections).

Preservation	• Keep separated from other items and store in a well-ventilated area. • Materials that absorb organic substances (activated charcoal is one such substance) should be added to the storage container. • Natural rubber items in an advanced stage of degradation should be packaged in an airtight low-oxygen environment (Ageless®). • Foam rubber objects must be supported and sheets of rubber should be separated from each other using a non-adherent inert material. • RH 35–45%, temperature < 18 °C.

History

Two thousand years ago, the indigenous peoples in the jungles of South America made shoe soles from the “weeping tree’s tears” (the word *cahuchu* translated from a Brazilian indigenous people’s language)[23] and used it to coat fabrics and produce balls for playing games. Christopher Columbus was so fascinated by the latter that in the late 15th century he took a few of the balls with him back to Europe. It was regarded with amazement. Rubber was considered such a wonder that 16th century people thought it must originate from the body of a mythical beast. They were believed to have healing powers and used as a folk remedy to treat stomach ache and lung diseases. In the middle of the 18th century, European scientists learned about the origin, harvesting methods and applications of natural rubber. A period of rubber import started and inventors were supplied with this new material.[24]

Harvesting latex from a rubber tree in Cameroon. Sixty litres of latex yields 12 kg of natural rubber.

Scottish chemist Charles Macintosh was the first whose experiments led to profitable processing methods. He found that petrol dissolved natural rubber, and pouring the solution as a thin layer and letting the petrol evaporate left a sheet of rubber. Since it rained in Scotland on an average of 188 days a year[25], Macintosh realised that the substance could be used to produce a waterproof textile. In 1823, he patented a material consisting of a sheet of rubber pressed between two layers of fabric. Rubber raincoats were nicknamed macs after their inventor and enjoyed a brief period of success in the 1820s and 1830s, particularly in the military clothing sector. The unpleasant odour and instability of the rubber at different temperatures limited its success.[26]

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[23] DeMouthe 2006: 86.

[24] Palo-oja, Willberg 1998: 21–22.

[25] Current weather results and science facts.

[26] The Plastics Historical Society, 1851: Ebonite, the birth of the plastics industry?; Pickeral 2010: 279; Newton, Dubious durability? Two fashionable rubberised raincoats.

American amateur inventor Charles Goodyear devoted himself to addressing these material shortcomings. Often seen as a somewhat eccentric figure, his driving goal was to protect lives, notably by attempting to invent a life vest. Rubber seemed like a perfect material. After years of trial and error (he lacked chemistry training), Goodyear was able to stabilise the material by treating it with sulphur. This was a milestone in plastics and rubbers – vulcanised rubber was patented in the US in 1844. In a dramatic twist, the Englishman Thomas Hancock patented the same method in his own native country a month before Goodyear. It is still unsettled which of them really invented vulcanisation.[27]

Chemically speaking, vulcanisation refers to the cross-linking of polymer chains in rubber, transforming it into a thermoset.[28] At the Great Exhibition of 1851 held at the Crystal Palace in Hyde Park, England, Goodyear (who had declared personal bankruptcy in 1830) spent US $30,000 to display giant balloons, boats, footwear, furniture and medical instruments, all made of rubber.[29]

Products

Natural rubber is mainly used to produce elastic products: conveyor belts, hoses, seals, shock absorbers, carpets, coatings, inflatable products (boats and mattresses), protective gear (masks, gloves), footwear, medical and health supplies (bags, pacifiers, probes) and commodities (balls and toys). Upholstery, mattresses and many foam rubber toys familiar from childhood are made of foam rubber.

Hard rubber continues to be produced under brand names such as Ebonite or Vulcanite. Ordinary vulcanised rubber (such as in automobile tyres) has a sulphur content of 2–3%, while sulphur content can be up to 32% in hard rubber.[30] This high-sulphur material can be polished and fashioned into objects that imitate ebony or jet, such as buttons, jewellery, ink pots, musical instruments, and combs.

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[27] The Plastics Historical Society, Goodyear.
[28] Christjanson 2010: 10–11; The Plastics Historical Society, Charles Goodyear (1800–1860).
[29] FineArtAmerica.
[30] Brydson 1999 [1966]: 838.

E. Haavik, a foreman at the Tegur rubber factory, with a basketball being manufactured on an experimental vulcanisation machine, 1962. Photograph: I. Prooso. EFA.250.0-25493

Products made by the Tegur rubber factory in 1973. Photograph: E. Tarkpea. EFA.204.0-96364

A comb made of vulcanite (1920s). Photograph: Berta Jänes, Anu Ansu. ERM A 718:115

2.1.2. Nitrocellulose (celluloid)

Abbreviation	NC
Category	Thermoplastic
Discovered by	1846 – Christian Friedrich Schönbein, Switzerland (explosive) 1862 – Alexander Parkes, England 1868 – John Wesley and Isaiah Hyatt, USA
Derived from	Cellulose fibres reacting with concentrated nitric and sulphuric acids. Camphor and additives are added to the end result.
Production	Product samples were introduced in London in 1862, and production began in 1866. (England). From 1884, it was in use as a textile (Chardonnet silk). Photographic film and negatives from 1889 to 1950.
Examples of product names	Pyroxylin (1846), Parkesine (England, 1862–1868), Xylonite (England, 1868), Celluloid (USA, 1872), Durofix, Duco cement.
Production methods	Blow moulding, cutting sheets from a block, stamping, thermoforming.
Solvents	Mixture of ethanol and ether, acetone, concentrated acids.
Glass transition temperature	T_g = 53–56 °C
Melting point	T_m = 80 °C
Rigidity	Rigid, can be modified with plasticisers.
Density	$\rho = 0.77\ g/cm^3$
Colour	Any colour
Transparency	Transparent, takes on a light yellowish tone as it ages.
Refractive index	$n = 1.51$
Odour	Reminiscent of pine resin.
Usage	Household items, rolls of film, photographic negatives, textile fibres, table tennis balls (until the 2020s, at which point it was replaced with ABS, since nitrocellulose is flammable).
Pros	• Good impact strength. • Easy to mould. • Lightweight.
Cons	• Vulnerable to solvents. • Unstable – gives off acidic compounds as it ages (damages other materials). • Flammable.
Ageing	• Objects crack (all the way through the object) and crumble. • Hydrolysis – items become acidic and give off acidic compounds • Additive migration – over time, camphor migrates to the surface and vaporizes. • Causes corrosion of metals it comes into contact with. • **Malignant plastic!** (hazardous to other items in museum collections).
Preservation	• Stable, well-ventilated environment. Acid-absorbents (activated charcoal and zeolites) should be added to packages. • Keep separated from other items in museum collections. • Pay special attention to nitrate film stock because of fire hazard. • RH 35–40%, temperature < 15 °C.

History

The first semi-synthetic plastic – nitrocellulose – was developed by the Swiss chemist Christian Friedrich Schönbein in 1846. According to legend, Schönbein spilled a very corrosive mixture of concentrated sulphuric and nitric acid on his desk. Without thinking, he grabbed a cotton apron and wiped up the spill. He rinsed out his wife's apron, hung it to dry by the stove, but it ignited and vanished with a bright flash. He had discovered a substitute for gunpowder.[31] Guncotton was three times more powerful than its predecessor and didn't give off the dark smoke that made shooters' eyes sting and interfered with aiming. Guncotton was also much more stable than the notorious nitroglycerine, which could explode if merely shaken.[32]

A mixture of nitric and sulphuric acids could dissolve cellulose, otherwise insoluble. It wasn't possible to melt and mould the end product, as it was extremely explosive. In the early 1860s, the English inventor and metal artist Alexander Parkes succeeded in developing a method for making guncotton less unstable, using various oils and waxes. The new material could be heated and moulded. At the London Great International Exhibition of 1862, Parkes unveiled a synthetic ivory, the first semi-synthetic plastic. It was given the commercial name of Parkesine in honour of its inventor.[33] Parkesine could have a hard finish like horn, or be stretchable like leather. Transparent in pure form, it could be tinted with pigments and fillers.

At the same time that Parkes was tinkering with the invention of his new material, a newspaper across the Atlantic ran an ad – one of America's biggest billiard supply companies was looking for an alternative material to costly ivory. Billiards had become a modern pastime for affluent gentlemen in the late 19th century. But the fad pushed Indian elephants (African elephant tusks were generally not used) to the brink of extinction, as only 4–5 balls could be made from each tusk. (English billiards required three balls.) The ad offered a prize of US $10,000, which spurred John Wesley Hyatt and his brother Isaiah into action. John, who worked at a printer's shop, noticed that the colloidal solution (nitrocellulose, ether and alcohol solution) used to repair small tears occurring in the printing process, dried into a material as hard as ivory. He developed a method for applying a thick layer of colloid onto a sphere made of compressed paper and shellac. Although they won the competition, the brothers never received the prize money. The Hyatts could at least take credit for inventing a plastic superior to Parkesine, and enjoyed commercial success.[34] In 1868, the artificial ivory billiard balls developed by the Hyatts were already in production.

However, this was not an ideal material, either: these balls were liable to explode. According to one legend, Hyatt received a letter from the owner of a billiard saloon in Colorado who was concerned not so much about the loud explosions themselves, but the

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[31] Mossman 2008: 35.

[32] Painter, Coleman 2009: 6; Beall, Plastics Hall of Fame ...

[33] Mossman, Parkesine & Celluloid.

[34] Painter, Coleman 2009: 9.

reactions from the trigger-happy patrons (this was back in the days of the Wild West). The Hyatts solved this problem in 1869 by adding camphor to the material.[35] In 1872, celluloid made its world debut.[36]

Products

Celluloid items entered mass production in both America and Great Britain in the 1870s. It was used to produce decorative boxes and toiletries, combs, jewellery, lamp shades, knick-knacks, frames for eyewear and parts of pens. These plastic items generally imitated much more pricey materials such as mother-of-pearl, ivory or tortoiseshell.[37]

Attempts were also made to produce false teeth made of celluloid. The compression and heating used to make the construction introduced residual stresses in the material, and over time the prosthetics became deformed. Hot foods and beverages were also problematic, considering that nitrocellulose softened at 80 °C. It also gave off a taste of camphor, which was a nuisance.[38] (And just think of the risk posed to smokers!)

Celluloid collars and cuffs, produced from the 1880s on, enjoyed greater success. Even though they cost the same as fabric versions, care and maintenance was easier. Cotton collars had to be washed, starched and pressed, and it was hard to keep them looking brilliant white. Celluloid collars were durable and easy to clean. The most popular manufacturing method used lamination: a layer of cotton cloth sandwiched between two thin sheets of celluloid. In the 1930s, fashions changed and the popularity of celluloid shirt collars declined sharply.[39]

A silk made of nitrocellulose fibres introduced at the 1889 Paris Exposition was a sensation. It was named Chardonnet silk after its inventor, Louis Marie Hilaire Bernigaud, the Count of Chardonnet. Many women were enthralled and wore haute couture dresses made of the synthetic silk. Unfortunately, when near open flame, these garments, too, could become even more ra-

Advertisement for a nitrocellulose shirt collar and cuffs (ca 1870–1900). Photograph: Digital Commonwealth

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[35] Camphor is a flammable, waxy, transparent crystalline terpenoid with a distinctive and strong odour. It is obtained from two trees – Cinnamomum camphora and Dryobalonops aromatica (Wikipedia. Camphor).

[36] Brydson 1999: 4.

[37] Mossman, Parkesine & Celluloid.

[38] Brown, Plastics in Dentistry 1.

[39] The Plastics Collection, White Collar Plastic.

diant, so to speak, due to the flammability of nitrocellulose, and Chardonnet's silk was given the nickname "mother-in-law silk".[40] The Count of Chardonnet solved this problem by denitrifying the nitrocellulose fibre – the fibre was treated with an aqueous solution of ammonium hydrosulphide. Chardonnet silk was produced until the 1940s.[41]

In the late 1880s, the Hyatts found that celluloid could be used as photographic negative stock. An agreement was signed with George Eastman, and Kodak's rolls of transparent celluloid film for photographs appeared in American stores in the autumn of 1889.[42] Cinematic films also began to be shot on nitrate film. Production of nitrate films ceased in the 1950s, since they were very flammable and had caused a number of catastrophic fires in cinemas, film archives units and even in hospitals (nitrocellulose was the base for X-ray films).

Nitrocellulose is very common in museum collections. Compared to other materials, items made of it are lighter, thinner and more detailed. Celluloid items often have a glossy surface and give off a characteristic sound when tapped gently.

In addition to varnishes, nitrocellulose is still in use today as a plastic. It is firmly established as a material for laminating accordions and the bodies of guitars.

A sun visor. Photograph: Anu Ansu and Berta Jänes. Author's collection of samples

A celluloid comb, Tartu Comb Factory, 1959. Photograph: Anu Ansu and Berta Jänes. ERM D 100:29

A celluloid toy elephant. ERM A 800:19

A celluloid fan. ERM A 802:52

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[40] Mossman, Synthetic Fibres, From Dreams To Reality.
[41] Painter, Coleman 2009: 10.
[42] Harding, Celluloid and Photography.

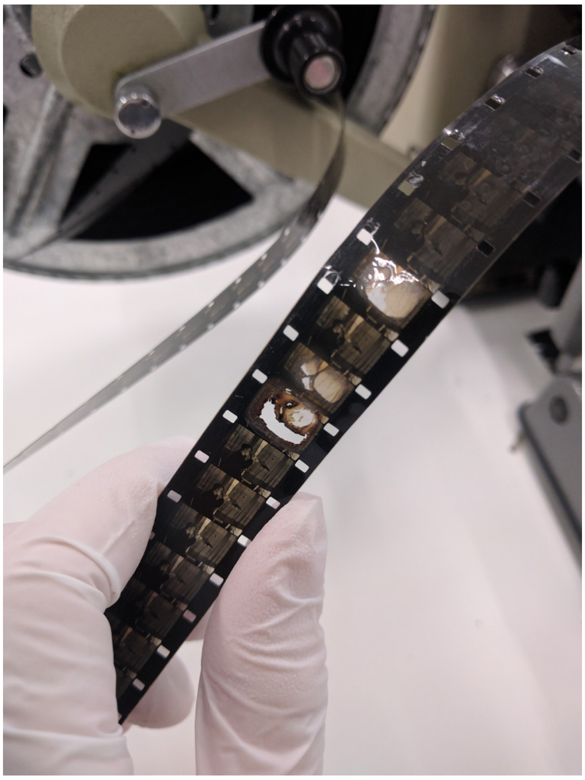
2.1.3. Cellulose acetate

Abbreviation	CA
Category	Thermoplastic
Discovered by	1865 – Paul Schützenberger, France 1905 – George Miles, USA 1913 – Camille and Henri Dreyfus, Switzerland (acetate fibre)
Derived from	Reaction between cotton pulp and a mixture of acetic acid and acetic anhydride. The product, a white powder, is then dissolved in acetone, and plasticisers (phthalates), stabilisers and pigments are added.
Production	Photographic film made from 1908 (Kodak), acetate fabric made commercially from 1920, pelletised for commercial use starting from 1930.
Examples of product names	Setilithe, Tenite, Rhodoid, Kodacel, Celanese, Tricel.
Production methods	Pressing, injection moulding (from 1928), cutting sheets from a block, stamping, thermoforming.
Solvents	Acetone, organic solvents.
Glass transition temperature	T_g = 70–180 °C
Melting point	T_m = 210–300 °C
Rigidity	Rigid, can be modified with plasticisers. Good impact strength.
Density	$\rho = 1.3\ g/cm^3$
Colour	Any colour
Transparency	Transparent, becomes yellowish over time.
Refractive index	$n = 1.48$
Odour	Degraded plastic smells like vinegar.
Usage	Photographic film and negatives, consumer goods (frames for eyewear, eating utensils, pens, jewellery), toys and textile fibre.
Pros	• Easy to shape and tint. • Self-extinguishing. • Feels like a natural material to the touch.
Cons	• Hygroscopic, risk of hydrolysis. • Vulnerable to UV radiation.
Ageing	• Oxidation – UV radiation makes the transparent material turn yellowish quite quickly; objects become fragile. • Hydrolysis and migration of components – as it ages, acetate gives off acidic substances that react with moisture in the air to form acetic acid. Besides acidic compounds, plasticisers also migrate to the surface, making it sticky. The material shrinks due to the plasticiser loss and film-shaped products start curling and adhere to one another. • Older cellulose acetate items experience even more extensive age-related degradation, as the material often contains residual acidic catalysts due to peculiarities of historical production processes. • Causes corrosion of metals it comes into contact with. • **Malignant plastic!** (hazardous to other items in museum collections).

Preservation	• Stable, well-ventilated environment. Acid-absorbents (activated charcoal and zeolites) should be added to packages. • Keep separated from other items and store in a well-ventilated room. • Must not be exposed to UV light. • The storage environment must be neutral or mildly alkaline (acidic environments accelerate the emission of softeners). • RH 35–40%, temperature < 15 °C.

History

Cellulose acetate was first made by the French chemist Paul Schützenberger in 1865 by treating cotton fibres with acetic anhydride (anhydride of acetic acid). However, his product was unstable and hard to work with, and so it would be a few decades before the launch of commercial cellulose acetate production. It was not until 1905 that the American chemist George Miles developed a method for making the new semi-synthetic polymer soluble in acetone, through partial hydrolysis. In 1908, Eastman Kodak began producing “safety” films from cellulose acetate. During the First World War, the British impregnated fabric with cellulose acetate and used it to cover the fuselage of aircraft.[43]



In 1923, Kodak introduced 16 mm cellulose acetate film reels for amateur use. Photograph by the author

Manufacturing of cellulose acetate sheets and rods began in 1927, while the early 1930s saw the introduction of pelletised material. This was the first plastic used for commercial production using injection moulding. The new method made cellulose acetate a popular material for consumer goods, and until the second half of the 1940s, when polyethylene and polystyrene appeared, cellulose acetate remained the primary material for injection moulding.[44]

The term “cellulose acetate” can refer to any one of three related polymers: cellulose acetate, cellulose diacetate (from 1937 on) or cellulose triacetate (from 1947 on). The difference between them lies in the extent to which cellulose reacts with acetic anhydride. In acetate and diacetate, 75–92% of the cellulose hydroxyl groups have reacted, while

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[43] Brydson 1999 [1966]: 602; National Museum Of The U.S. Air Force, Sopwith F-1 Camel; Freemantle 2014: 313.
[44] The Plastics Historical Society, Cellulose Acetate.

the figure has to be over 92% for triacetate. The second withstands heat better than the first and the third better than the second, but the toughest is cellulose triacetate (T_m = 300 °C), next cellulose diacetate (Tm = 250 °C) and lastly cellulose acetate (T_m = 210 °C).[45] Diacetate and triacetate are mainly used for production of fibre and film tape.

Products

As already mentioned, cellulose acetate was used by the budding cinema industry as a substitute for nitrate film. While 16 mm and 8 mm acetate film quickly entered use in the amateur film world, 35 mm nitrate film long continued to remain in production in professional cinema. Only by the 1950s could nitrate film be considered truly retired, as manufacturing had ceased. The changeover was slow because nitrate film had superior image quality.[46] The next transition started slowly in the 1960s, when Kodak introduced polyester film stock.[47]

Cellulose acetate quickly achieved sales success in the manufacturing of consumer goods. The 1930s and 1940s brought cellulose acetate eyewear frames, pens, toothbrushes, hairpins and buckles. Use of cellulose acetate was particularly widespread during the Second World War, when it was used for items ranging from anti-aircraft rockets to buttons and buckles for military uniforms. A more salubrious, peacetime manufacturing sector was the toy industry. For example, Lego bricks, which rose sharply in popularity in the 1950s, were made of cellulose acetate until 1963.[48] The baton was then passed to ABS plastic (acrylonitrile butadiene styrene), which is frequently used in today’s toys. Eyeglass frames are still made from cellulose acetate today, despite the somewhat slow manufacturing method.[49] The end result is significantly more attractive than mass-produced polystyrene frames made by injection moulding. Cellulose acetate can be formed into a block composed of different layers and then cross-cut to create very striking patterns. This makes it possible to create patterns such as imitation tortoiseshell.

The production of acetate fibres, developed by Camille and Henri Dreyfus, began in 1910.[50] These fibres were woven into fabric marketed as acetate cloth (from 1925). At the same time other manufacturers produced viscose (also known as rayon) and it is common to mistake one for the other. Rayon and acetate are not actually synonymous, as the production method is different; acetic acid is used to manufacture acetate textile fibres. Consequently, the qualities of the textiles have slight variations. Viscose is more durable than acetate textile and absorbs more moisture (it dries more slowly). Acetate textiles are thermoplastic and thus also heat-sensitive (careful when ironing!).[51]

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[45] CIRFS – European Man-made Fibres Association.

[46] Nyback, … on Nitrate Film.

[47] Milestones, KODAK.

[48] Jaffe, Lego, the Ultimate Toy Building Brick.

[49] Morgan, Hampton, Acres, Cellulosics – A Classic Centenary; The Plastics Historical Society, Cellulose Acetate.

[50] Dinsmoor, Camille and Henry Dreyfus.

[51] Dinsmoor, Camille and Henry Dreyfus.

Sunglasses with frames of cellulose acetate. Photograph by the author

2.1.4. Casein formaldehyde (galalith)

Abbreviation	CF
Category	Thermoset
Discovered by	1897 – Wilhelm B. Krische and Adolf Spitteler, Germany.
Derived from	Casein from milk reacts with formaldehyde.
Production	In Europe from 1900 (never became popular in the USA). Use began declining in the 1960s.
Examples of product names	Lactoform (Germany), Galalith (France), Erinoid (England), Lactoid (England), Aladdinite (USA), Lactonit (Estonia, 1930s), artificial horn.
Production methods	Pressing, extrusion, stamping, machining, turning.
Solvents	(while heating) 1% potassium hydroxide, 5% ammonium chloride, 1% ammonium oxalate.
Vicat softening temperature	93.3 °C
Rigidity	Hard, slightly elastic.
Density	$\rho = 1.35\ g/cm^3$
Colour	Any colour.
Transparency	Cloudy, yellowish (not usually produced in transparent form).
Odour	When rubbed with a soft cloth smells cheesy/milky; when burned smells like scorched milk.
Usage	Knick-knacks: jewellery, buttons, pens, buckles, combs.
Pros	• Easy to tint. • Leads to an attractive polished end result. • Withstands solvents. • Can be reshaped to an extent after heating.
Cons	• Subject to the natural precursor. • Hygroscopic. • Thermophobic.
Ageing	• Hydrolysis – crazes, crumbles. • Thermo-oxidation. • Sudden temperature changes cause crazing. • Mould/mildew risk.
Preservation	• Avoid sudden temperature and relative humidity shifts. • Must not come into direct contact with water (hygroscopic material!) • RH 50–55%, temperature < 18 °C.

History

Inspired by the idea that it was possible to create materials never seen before and the fact that nitrocellulose introduced in the 1860s was far from a perfect plastic, the quest for an ideal, scalable commercial material continued. These attempts went on for nearly 40 years.[52]

In the second half of the 1890s, German schools had demand for whiteboards to replace the traditional blackboards. The solution was found in 1897 as a result of the collaboration between printing house director Wilhelm B. Krische and the chemist Adolf Spitteler. A suitable plastic was produced from milk protein (casein) soaked in formaldehyde.[53] Truth be told, it wasn't a totally brand-new innovation – back in the 2nd millennium BC, casein had been used in Ancient Egypt as a pigment binder in paint. And the fact that cheese hardens over time when exposed to the air, has probably been discovered by most people. Already in the 16th century, a Bavarian monk fashioned an artificial horn from casein treated with an alkaline solution of ash and water.[54] The new innovation in the late 19th century was the use of formaldehyde, which made the milk protein chemically and biologically more resistant. What led Krische and Spitteler to use formaldehyde? Perhaps it was the fact that formalin (an aqueous solution of formaldehyde) had been used for quite some time to preserve biological samples.

The new material was patented as Lactoform and it soon started to be competitive with nitrocellulose. Meanwhile, the French were also investigating casein. Galalith (from the Greek *gála* for milk and *-líthos* for stone) was introduced at the 1900 Paris International Exposition. As in the case of celluloid, Galalith was originally capitalised as a brand name but later became the common term for hardened casein.[55] In Estonia, galalith production gained impetus in the 1930s thanks to the company A/S Eesti Kunstsarve Tehased O. Kerson and Ko. (Kerson & Co. Artificial Horn Factories). The products of this company were among the top three in Europe, competing with England and Germany. Locally made casein formaldehyde was marketed under the brand name Lactonit.[56]

Stamping button blanks in 1948. Photograph: V. Samussenko. EFA.204.0-1790

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[52] Morgan 1999: 44–50.
[53] Morgan 1999: 44–50.
[54] Lang 1999.
[55] Galalith History.
[56] Erelt 2017.

Products

Product samples by A/S Eesti Kunstsarve Tehased O. Kerson & Co., mid to late 1930. Pekka Erelt's private collection

A major plus of galalith is the very wide range of possible colours. It can be white, black, pastel, vivid or glittery. The plastic itself is transparent but it was not produced in its pure form. Often it imitated ivory, marble, mother-of-pearl, ebony and horn. The product was made mechanically from a rod, leaf or block. Buttons became the main commercial article (by 1926, 55% of buttons in the world were made of galalith[57]). It was also used for combs, jewellery, eating utensils, knitting needles and pens.[58]

It remained a popular plastic for the production of buttons in Europe until the 1970s. It was then joined by polyester, which was significantly easier to process. Nor did polyester require an expensive natural precursor. In the Soviet Union, galalith fell out of popularity already in the 1960s, as in 1962, the Central Committee of the Communist Party adopted a decision to reduce the use of raw food products within the technological sector; as a result, casein became scarce.[59] Interestingly, galalith never became popular in the US. Perhaps climatic conditions in many areas were unsuitable for production or use (too dry or too humid).[60]

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[57] Ralston, Osswald, The History of Tomorrow's Materials ...
[58] The Plastics Historical Society, From Milk to Manicure Sets ...
[59] Lageda, Kanne 1968: 38.
[60] The Plastics Historical Society, From Milk to Manicure Sets...

2.2. Synthetic plastics

2.2.1. Phenol formaldehyde (Bakelite)

Abbreviation	PF
Category	Thermoset
Discovered by	1907 – Leo Hendrik Baekeland, USA.
Derived from	Phenol (a crystalline substance used in 5% solution as an antiseptic) reacts with formalin (aqueous solution of formaldehyde).
Production	From 1910 to the present day. From 1928 as a transparent resin.
Examples of product names	Bakelite, Resinol, Phenodur, Catalin, Mouldrite, Nestorite, Roanoid, Cravacraft.
Production methods	Moulding, pressing, stamping, turning.
Solvents	Concentrated mineral acids and bases.
Decomposition temperature	~300 °C
Rigidity	A very rigid plastic.
Density	Without fillers: $\rho = 1.40$ g/cm^3 With cellulose fillers: $\rho = 1.58$ g/cm^3
Colour	Dark (black, brown, greenish, reddish), transparent (without fillers).
Transparency	Transparent, yellowish-brown tone.
Refractive index	$n = 1.47–1.50$
Odour	Medicinal, reminiscent of antiseptic.
Usage	Initially for electrical insulation, then electrical appliance housing, knick-knacks, automotive industry, varnishes and adhesives.
Pros	• Good mechanical resistance and dielectric properties. • Good resistance to temperature fluctuations and high temperatures (does not melt). • Mechanical properties can be modified with various fillers • Resistant to chemicals and solvents. • Easy to mould.
Cons	• Limited colour range (only dark tones). • When not tinted, rapidly becomes yellowish. • Brittle. • Bakelite, which contains organic fillers (sawdust, cotton fibre, paper, textile) is hygroscopic – mould and mildew risk.
Ageing	• Bakelite withstands ageing well. A problem may become evident if the object has been in damp conditions for some time. Cellulose fillers added to the polymer mixture absorb moisture. Microcracks appear in brittle plastic and affect the durability of the plastic. • Photo-oxidation – colour becomes pale, yellowish.
Preservation	• Avoid direct sunlight and extended exposure to water. • RH 35–45%, temperature < 23 °C.

History

The 20th century brought a new miracle worker to help with everyday chores – electricity. The "clean light" that started replacing sooty oil and gas lanterns in the late 1910s became more norm than novelty in middle-class homes in the second decade of the 20th century. But light wasn't the only thing that electricity made possible. The era of electrical appliances had dawned. The iron, the water heater, toaster, hair dryer, vacuum cleaner, electric radiator, telephone, radio – all of these everyday items came into use less than a century ago thanks to electricity.

It is naïve to think that people managed to tame such a powerful force immediately. In the beginning, it did not occur to people to insulate electrical wiring. As death notices cropped up in newspapers due to electrocution, the first attempts to prevent electrocution were with paper and lead. Strips of cloth and wood were also used as insulators. Then came the idea of using vulcanised rubber. Eventually, shellac became standard.[61]

Shellac is obtained from a sap secreted by a species of beetle in the tropics and subtropics (*Laccifer lacca*). Production is labour-intensive and time-consuming – it would take 15,000 beetles six months to secrete enough shellac to yield 500 grams of flakes. This quantity and rate of production had previously been sufficient. But after shellac became the main insulator for electrical wiring and equipment, demand outstripped production and the price soared.[62] A synthetic alternative to shellac was needed.

Shellac samples in different hues. Photographs: Anu Ansu and Berta Jänes

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[61] Phillips, Lipscomb 2013.
[62] Tradish 2004: 27–35.

Along with many other scientists, Leo Hendrik Baekeland, a chemist of Belgian origin based in the US, set to work on finding a solution. He noticed that a mixture of phenol and formaldehyde formed a sticky mass that became especially strong after being heated, cooled and then dried. As he continued his research, Baekeland discovered that the material could be mixed with wood powder and slate dust to form composite materials with different qualities. Most of the products were hard and fire-resistant. The only flaw was that the new material started frothing during production and the end result was substandard. Baekeland fashioned a pressurised vessel – patented as a "bakelizer" – that forced the bubbles out of the polymer mixture. In 1907, Baekeland was issued a patent for the phenol formaldehyde production method he had developed.[63] In February 1909, Baekeland unveiled the first completely synthetic thermoset that could be produced on an industrial scale – Bakelite.[64]

Products

At first, phenol formaldehyde was used for the purpose for which it was originally developed – an insulator for electrical wiring and other conductors. Bakelite also saw widespread use as a varnish. Retail products made of Bakelite appeared in the 1920s and 1930s, radios being among the first as Bakelite was a perfect material for their casing. Other enclosures around electrical appliances were also made of Bakelite (blow dryers, electric razors) as well as telephones, tableware and automotive parts. Closer to the present day, we see Bakelite in frying pan handles, control dials on stoves, handles of conventional irons and soldering irons. Bakelite had become a "material of a thousand uses", as Baekeland himself had touted.[65]

Radio with bakelite housing, model EKCO AD76, from 1935. ERM A 941:37

Bakelite items from the author's collection of samples. Photographs: Anu Ansu and Berta Jänes

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[63] American Chemical Society, The Bakelizer.
[64] The Plastics Historical Society, Baekeland and Swinburne.
[65] Shashoua 2008: 26.

Catalin

In 1927, Baekeland's Bakelite production patent expired. In the same year, the American Catalin Company developed a purified form of phenol–formaldehyde resin. Catalin, that did not use fillers. It could be dyed 20 different shades of colour. Producers sold rods, plates or blocks of Catalin to craftsmen and factories where they were hand-crafted or machine processed into attractive jewellery, pens, or knife and fork handles.[66] Busy housewives could also make napkin rings at home by buying Catalin kits made specifically for this purpose.[67] Catalin radio cabinets and tabletop clocks proved very successful.

A Fada brand radio with housing made of Catalin plastic, late 1930s. Photograph: radios10467, Ebay

Catalin items are generally brightly coloured and translucent. However, the lack of fillers meant the phenol resin was fragile. As it ages, Catalin shrinks. There are also problems with the colour – bright colours become duller. This is primarily caused by smoke, dirt, dust and sunlight. White becomes yellowish or even orange, bright *lapis lazuli* becomes seaweed green, emerald turns a dark-beer colour. Fortunately, the phenol alcohol, a constituent of the plastic, keeps UV light from penetrating into the material, so the deterioration remains superficial.[68]

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[66] Holdsworth, Cast Phenolic Resin.
[67] Clark, A–Z of Animal Napkin Rings.
[68] Holdsworth, Cast Phenolic Resin.

2.2.2. Amino plastics

Urea formaldehyde	
Abbreviation	UF
Category	Thermoset
Discovered by	1919 – Hanns John, Prague. Early 1920s – Kurt Ripper and Fritz Pollac, Germany
Derived from	Reaction between urea and an aqueous solution of formaldehyde (formalin).
Production	From 1925 England. Still in use today.
Examples of product names	Beetle, Bandalasta, LingaLonga, Plaskon, Scarb, Pollopas.
Production methods	Injection moulding, transfer moulding.
Solvents	Concentrated acids and bases.
Rigidity	Rigid.
Density	(with cellulose fillers) $\rho = 1.47–1.52$ g/cm^3
Colour	Pastel tones, all colours.
Transparency	Opaque.
Usage	Switches, plugs, sockets, insulation, electrical appliance casings, table-ware, jewellery, varnishes, paints.
Pros	• Possibility of manufacturing in light colours. • Items are hard; reminiscent of ceramics. • Good resistance to heat and cold. • Resistant to chemicals. • Not electrostatic (does not attract dust).
Cons	• Fades through exposure to UV light. • Sensitive to moisture (cellulose fillers). • Heavy. • Fragile (must be reinforced with fillers).
Ageing	• Becomes cracked and delaminated due to moisture and sudden temperature changes. • Risk of mould. • Becomes yellowish brown when exposed to high temperatures.
Preservation	• Avoid direct sunlight and extended exposure to water. • RH 35–45%, temperature < 23 °C.

Melamine formaldehyde	
Abbreviation	MF
Category	Thermoset
Discovered by	1936 – William F. Talbot, USA.
Derived from	Reaction between melamine (a white, organic, alkaline substance, flame retardant) and an aqueous solution of formaldehyde (formalin).
Production	Late 1930s, particularly popular starting in the 1950s. Still widely used today.
Examples of product names	Hornitex, Melmex, Formica (countertops, panels), Melopas, Argosy, Gaydon, Melaware, Bootonware, Melmac.
Production methods	Injection moulding, transfer moulding.
Solvents	Concentrated acids and bases.
Rigidity	Rigid.
Colour	Pastel tones, all colours; often two-coloured.
Transparency	Opaque.
Usage	Household items, tableware, adhesive for wood chip boards, coating on countertops (Formica), varnishes, adhesives.
Pros	• Items are hard; reminiscent of ceramics. • Moisture proof. • Resistance to lower and higher temperatures. • Good resistance to chemicals. • Mechanically more resistant than urea formaldehyde (less moisture sensitive). • Not electrostatic (does not attract dust).
Cons	• Heavy (compared to other plastics). • Fragile (must be reinforced with fillers).
Ageing	• Becomes yellowish brown when exposed to high temperatures. • Melamine tableware must not be used for heating food in a microwave. Not because of a health hazard, but because the heat of the microwaves damages the fillers in the plastic. Exposure to microwaves will significantly shorten the lifespan of the dish.
Preservation	• RH 35–45%, temperature < 23 °C.

History

In 1919, a patent for the manufacture of urea formaldehyde was awarded to Hanns John in Prague. The properties of the new plastic were largely similar to those of phenol formaldehyde, but it could be produced in light pastel tones. In Great Britain, manufacturing started in 1925. In the late 1930s, urea formaldehyde was joined by another amino plastic – melamine formaldehyde (MF). It was superior to its predecessor and quickly superseded it.[69]

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[69] Quye, Williamson, 1999: 152.

Items made of melamine only became popular in American homes after the Second World War, but by the 1950s, melamine tableware was such a hit that porcelain and ceramics makers revolted. Defamation, counter-propaganda, demonstrations – they tried everything to prevent plastic from triumphing over the old, traditional material. It was a losing battle, because melamine dishes were lightweight, unbreakable, brightly coloured with striking designs and considered stylish.[70]

Products

Initially, urea formaldehyde was used mainly to produce switches, plugs and sockets, as it was a good insulator. It was then tested for possible use in tableware and household accessories. Although it was easy to produce the items, they were not very successful. The problem was that the material wasn't waterproof. Wood dust or wood fibre was used as the filler, which expanded in contact with moisture and then contracted again. This caused the dishes to crack quite quickly.[71]

In the late 1930s, melamine formaldehyde switched places with its inferior predecessor. The fillers in melamine were mineral in origin, making the new material more resistant to heat, moisture and acids and mechanically stronger. At the same time, the colour did not fade as fast. During the Second World War, the US Navy put in gigantic orders for tableware because the material was perfect for their needs – it was waterproof, unbreakable and lightweight compared to metal or ceramics.[72]

Set of Oneida cups from the 1950s. Photograph: Laser Rosenberg

After the war, melamine took over in homes – utensil handles, cups, trays, bowls and thermoses were all made of it. Melamine laminated countertops (manufactured by Formica in the USA) became the key stylistic feature in kitchens and diners in the 1950s and 1960s. For the first time, pastel or multicoloured heat-resistant, scratch-resistant panels could be produced, and compared to solid wood panels, were much easier to maintain. Ease of maintenance was particularly important. In the early 1960s, the American civil rights movement began, and domestic servants, who were often Black, began to leave middle-class housewives to shoulder the task of cleaning, cooking, taking care of the family and entertaining guests. Low-maintenance plastic tableware, containers and countertops were thus a godsend and known as "the housewives' saviour".[73] Even today, wood particle boards, clothing and paper are permeated with liquid resins. Amino plastics are also used to make wood glue and weather-resistant varnishes and paints.

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[70] Akhurst, The Rise and Fall of Melamine Tableware.

[71] Wahlberg 1994: 14.

[72] Wahlberg 1994: 15.

[73] Katz, Formica Laminate Design.

2.2.3. Polystyrene

Abbreviation	PS
Category	Thermoplastic
Discovered by	1839 – Eduard Simon, Germany. 1866 – Marcelin Berthelot, France. 1931 – chemical manufacturer I.G. Farbenindustrie, Germany.
Derived from	Polymerisation of styrene (phenylethene, a sweet smelling, volatile, colourless liquid). Styrene is derived from petroleum.
Production	Commercially since the 1930s (Germany, UK, USA). Sweden launched production of extruded polystyrene foam (XPS) in the 1930s. 1954 – Expanded polystyrene foam (EPS) (USA).
Examples of product names	Vestyron, Polystyrol, Carinex, Hostyron, Styron, Lustrex, Sicostirol, Styrofoam, Penoplast, Lacqrene.
Production methods	Injection moulding, extrusion, thermoforming, casting.
Solvents	Acetic acid, acetone, benzene, chloroform, formic acid, hydrogen peroxide (30%), nitric acid (70%), petrol, toluene, xylene, turpentine.
Glass transition temperature	$T_g = 100$ °C
Melting point	$T_m = 240–290$ °C
Rigidity	Hard, rigid.
Density	$\rho = 1.04–1.05$ g/cm^3
Colour	Any colour.
Transparency	Transparent.
Refractive index	$n = 1.59$
Usage	In the late 1940s, polystyrene became a principal material for disposable consumer goods (such as pens, razors and packaging). Because of its transparency, it is used instead of glass for eyewear lenses. In foamed form, it is used to package fragile items (eggs, electronics) and in containers for hot food, and thermal insulation in the construction industry.
Pros	• Excellent transparency. • Easy to shape, cheap. • Can be modified with various rubbers to create tougher plastics with high impact strength (HIPS, ABS).
Cons	• The rigidity and hardness of pure polystyrene may be a problem as the material does not tolerate impacts, and cracks/fragments easily. • Low glass transition temperature, due to which it cannot be used at temperatures higher than 90 °C. • Poor resistance in outdoor conditions. • Electrostatic – attracts dust.
Ageing	• Photo-oxidation – fragile, becomes yellowish. • Burns with a sooty flame, gives off toxic substances.
Preservation	• Avoid direct sunlight. • RH 35–45%, temperature < 23 °C.

History

Styrene was first mentioned in scientific literature in 1831 by Jean-François Bonastre. However, it was not in use until 100 years later, in 1930s Germany. During the Second World War, the vast majority of production was geared towards making synthetic rubber. Thereafter, polystyrene became a widely produced plastic, without which it would be difficult to imagine packaging and construction.

Polystyrene products are diverse. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

Products

Polystyrene is produced through radical or ionic polymerisation of styrene, a colourless liquid. The main drawback of the product is its fragility, which can be reduced by adding synthetic rubber (1–10%). This results in high impact polystyrene (HIPS), which is used for helmets, toys, sports equipment, and radio and electrical housings. Extruded polystyrene (XPS, brand name Styrofoam) has been used in fast-food takeout containers and egg cartons (banned in the EU as of summer 2023). Expanded polystyrene (EPS, known as penoplast in Estonia) is used as thermal insulation and for packaging fragile items.[74]

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[74] Birley, Heath, Scott 1988: 50.

A fourth modification is also common – acrylonitrile butadiene styrene or ABS. ABS is a strong, rigid plastic with high tolerance to impact and stress fractures and has good chemical resistance.[75] ABS is a favourite material for the toy industry, and can be used for example to make durable action figures, dolls, Lego bricks and toy guns.

Since polystyrene has good transparency, it is also used instead of glass. It is turned into eyewear lenses, coloured wall tiles, radio casings, toys, photo supplies, haberdashery (buttons, combs, jewellery), furniture buttons, electrical switches and office supplies. The packaging industry found the transparent casing is well suited for displaying package contents to consumers. It should be mentioned that in recent years transparent PS packaging has started to be replaced with polyethylene terephthalate (PET, PETE) because of its significantly more lucrative and simpler recycling possibilities.

An Imula radio, 1990s. ERM A 957:16

Foam “peanuts” for the safe transport of fragile items are made from extruded polystyrene (XPS) and expanded polystyrene (EPS). Photographs: Anu Ansu and Berta Jänes

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[75] Birley, Heath, Scott 1988: 55.

2.2.4. Polyamide (Nylon)

Abbreviation	PA
Category	Thermoplastic
Discovered by	1935 – Wallace Carothers, USA.
Derived from	Polycondensation of dicarboxylic acids and diamines. Derived from petroleum.
Production	PA 6.6 from 1938 in fibre form (USA, Germany from 1939), from 1941 as moulding powder (USA).
Examples of product names	Nylon, Akulon (Netherlands), Capron (USA), Kapron (USSR), Rilsan (France), Grilon (Switzerland), Maranyl (UK), Durethan (Germany), Ultramid (Germany), Vestamid (Germany).
Production methods	Extrusion, injection moulding, rotational moulding, casting.
Solvents	Phenols, concentrated acids.
Glass transition temperature	PA 6 and PA 6.6: $T_g = 43–53$ °C
Melting point	PA 6: $T_m = 220$ °C PA 6.6: $T_m = 255$ °C
Rigidity	Rigid, tough.
Density	PA 6: $\rho = 1.13$ g/cm^3 PA 6.6: $\rho = 1.14$ g/cm^3
Colour	Any colour.
Transparency	Transparent, yellowish tone.
Refractive index	$n = 1.53$
Usage	Components that must tolerate high loads and friction, filament for textile production (stockings, parachutes, sportswear), toothbrush bristles.
Pros	• Very good mechanical resistance to wear. • Good resistance to high temperatures. • Good resistance to chemicals. • Good dielectric properties. • Textiles are easily dyed.
Cons	• Hygroscopic, which reduces the mechanical resistance of the material. • Along with moisture, the material also absorbs various tannins and pigments, which can lead to undesirable stains. • Vulnerable to UV radiation.
Ageing	• Photo-oxidation – the material becomes more fragile and yellowish. • Hydrolysis (PA 6.6 is most affected).
Preservation	• Avoid direct sunlight and exposure to water. • RH 35–45%, temperature < 23 °C.

History

In 1939, an item for everyday use appeared on the shelves in the US, which despite the ensuing war, made people smile a little more confidently – a toothbrush with synthetic bristles, namely Dr. West's Miracle-Tuft Toothbrush. The evolutionary leap from bacteria-harbouring wild boar hair and horsehair to hygienic brushes was made possible due to the experiments at DuPont led by the American chemist Wallace Carothers. A team of top chemists spent 12 years looking for a way of producing synthetic silk. In 1938, DuPont unveiled a filament that had cost US $27 million to research – Fiber 66. It took DuPont over two years to come up with a good trade name: Nylon.[76]

Nylon is a polymer belonging to the polyamide (PA) family. There are many different polyamides (PA 6, PA 6.6, PA 6.10, PA 11, etc.). Polyamide was obtained by polycondensation of a dicarboxylic acid and diamine, and was first used to produce stockings. The repeating part of the molecular chain of both of nylon's components has six carbon atoms, which is denoted by the 6.6 added to the polymer's name. Polymer PA 6 was obtained by polymerisation of caprolactam, the result of which is a molecular chain whose repeating parts contain six carbon atoms.[77]

Products

Thanks to its heat resistance and strong durability, polyamides have seen wide use as mechanical components that can replace metal (e.g. car engine components) and are also used in the kitchen at home, e.g. spatulas. Synthetic fibres are a very important polyamide product. Although reminiscent of silk, nylon is mechanically much stronger.[78]

A polyamide spatula. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

A close-up of a spatula

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[76] Tradish 2004: 27–35.
[77] Whelan 1994: 314.
[78] Mauring 1985: 38.

At the World's Fair that opened in New York and San Francisco in the spring of 1939, women flocked to the DuPont booth, where a synthetic silk stocking was being demonstrated. The unprecedented satiny sheen and resistance to runs created great excitement. Nylon stockings officially went on sale in American stores on 15 May 1940 – a day that was even dubbed N-Day. All 750,000 pairs were sold out, thanks to months of advance advertising. Every consumer could only buy one pair of stockings. As a result, women came shopping together with their husbands and children in order to take advantage of the offer. Besides stockings, nylon underwear, socks, nightshirts, blouses, dresses and sportswear were also successfully marketed. Even a nylon wedding dress was made. Nylon changed the fashion industry forever.[79]

Unfortunately the outbreak of the Second World War meant that the entire polymer industry had to be directed toward the fight. From 1942–45, nylon was used mainly for parachutes and aircraft tyres. Stocking production was halted. Women had to fall back on their own resourcefulness. They used tinted creams or eyeliner to draw fashionable stripes on their moisturised legs to give the illusion of stockings. Beauty salons offered leg cosmetic services and cosmetic firms produced imitation stocking makeup. A pair of stockings might cost US $10–12 on the black market (the equivalent today of €127–154!). In one murder case at the time, a detective discounted the possibility that the motive was robbery, as several pairs of stockings found near the victim had not been stolen.[80]

When the war ended, the longed-for stockings returned to store shelves, and shoppers ran amok in American department stores in 1945 and 1946, since DuPont wasn't able to meet demand. Newspapers described the events akin to a war on the home front, with headlines such as "Nylon Sale and No Casualties" and "News Is All Bad on the Nylon Front".[81]

Sabiina brand polyamide stockings, AS SUVA, 1990s. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

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[79] MacKenzie, Marcozzi 2013: 3–4.
[80] Handley 1999: 45–46.
[81] Tradish 2004: 27–35.

2.2.5. Polymethyl methacrylate

Abbreviation	PMMA
Category	Thermoplastic
Discovered by	1901 – Otto Röhm, Germany. 1930 – Rowland Hill, John Crawford, England.
Derived from	Polymerisation of methyl methacrylate (colourless organic liquid) monomers. Derived from petroleum.
Production	From 1927 as a varnish (Germany), 1934 (UK), in the aviation industry during the Second World War, and a commercially mouldable material from the 1960s.
Examples of product names	Plexiglas (Germany), Perspex (UK), Lucite (USA), Acryloid, Altuglas, Oroglas, Diakon.
Production methods	Vacuum forming, casting, extrusion, injection moulding.
Solvents	Acetic acid, acetone, benzene, chloroform, formic acid, methyl alcohol, nitric acid (10% while heating, or 70%), toluene, xylene, vegetable oil, turpentine.
Glass transition temperature	Tg = 90–105 °C
Melting point	Tm = 200–290 °C
Rigidity	Rigid and fragile.
Density	ρ = 1.17–1.20 g/cm^3
Colour	Any colour.
Transparency	Transparent.
Refractive index	n = 1.489
Usage	Glass substitute, varnishes, paints, adhesives, jewellery, dentures, furniture, panels.
Pros	• Excellent transparency. • Easy to thermoform.
Cons	• Fragile, shatters and cracks if struck hard or bent. • Vulnerable to many solvents. • Becomes brittle in the cold. • Fairly easy to scratch.
Ageing	• Tension cracking when exposed to solvents. • Photo-oxidation. • Hydrolysis.
Preservation	• Do not use solvents when cleaning. • RH 35–45%, temperature < 23 °C.

History

The German Otto Röhm is the first big name in the history of acrylic plastics. As early as 1901, he investigated how acrylates might be polymerised. In 1915, Röhm patented polyacrylic ester as a binder in paints.[82] The so-called acrylic glass has been produced since the 1930s. Germany and Britain pursued this avenue of research side by side. Röhm continued his research, attempting in the early 1930s to polymerize methyl methacrylate between two sheets of glass, in order to create a better safety glass. Much to his disappointment, the polymerised plastic separated from the panes of glass. But Röhm continued to work on this organic glass sheet, and his experiments culminated in 1933 in a product called Plexiglas. In England, polymethyl methacrylate was also discovered in conjunction with Röhm, by two chemists at Imperial Chemical Industries, Rowland Hill and John Crawford. ICI patented the invention under the name Perspex.[83] The new plastic went on sale in both countries in the late 1930s.

Acrylic glass was used during the Second World War to produce submarine periscopes and aircraft windscreens and window panes. Although used commercially to some extent before the war (for example in dentistry and for jewellery and doorknobs), PMMA came on the wider consumer market in the 1950s. Acrylate was primarily manufactured into sheets and rods, which companies would either thermoform, stamp or turn on a lathe.[84]

Products

Starting from the 1950s, acrylate was a popular material for jewellery and sculptures.[85] Today's "reuse" design movement was also topical back then – jewellery was made from residual material left over from aircraft windscreen production (Trifari Jelly Belly costume jewellery, Alfred Philippe).[86] In the 1960s, furniture designers used acrylic as an illustration of the space age. It allowed for the creation of transparent, lightweight and strong furniture, not possible with glass. Examples include Eero Aarnio's *Bubble Chair* from 1968 and Philippe Starck's *Ghost Chair* from 2002, now design classics.

Due to its transparency and durability, acrylate was a good material for motorcycle helmet visors. In the second half of the 1960s, helmets became mandatory in the Soviet Union. In the Estonian SSR, large-scale helmet production was launched at the company Salvo, and it was the company's main product by the end of the decade. The helmet shells were made of high-impact polystyrene or polyethylene and later polycarbonate as well.

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[82] The Plastics Historical Society, Rohm and Haas.
[83] Encyclopaedia Britannica, Polymethyl Methacrylate.
[84] The Plastics Historical Society, Polymethyl Methacrylate.
[85] Rivenc, Richardson, Learner 2011.
[86] Ebay, Antique Jewellery: What is a Jelly Belly Anyway.

Eero Aarnio bubble chair, 1968. Photograph: Hans B.

A Louis Ghost (Kartell) – a ghost chair designed by Philippe Starck, 2002. Photograph: Starck Ting

Motorcycle helmet, 1970s. The visor is made from PMMA, and the shell is made from ABS. ESM Fp 560:164 S 1809

2.2.6. Polyvinyl chloride

Abbreviation	PVC (plasticised PVC-P, unplasticised PVC-U).
Category	Thermoplastic
Discovered by	1835 – Henri Victor Regnault, France (monomer). 1912 – Ivan Ostromyslensky, Russia. 1926 – Waldo Semon, USA.
Derived from	Polymerisation of vinyl chloride monomer. Derived from petroleum.
Production	Commercial and industrial use since 1930 (PVC-P – sheets of film, insulation around cables and conductors, PVC-U – water and sewerage pipes, Germany). Pelletised for production of toys and industrial goods since 1940.
Examples of product names	Varlan, Hostalit, Vestolit, Varina, Solvic, Breon, Vipla, Excelon, Tedlar, Trovicel, Tygon, Verilon, Darvic, Welvic.
Production methods	Injection moulding, extrusion, calendering, thermoforming, rotational moulding.
Solvents	Acetone, benzene, chloroform, nitric acid (70%), toluene, xylene.
Glass transition temperature	PVC-P: Tg varies depending on content of plasticising agent PVC-U: $T_g = 81$ °C
Melting point	PVC-P: Tm varies depending on content of plasticising agent PVC-U: $T_m = 175$ °C
Rigidity	PVC-P – elastic PVC-U – rigid and hard
Density	PVC-P: $\rho = 1.18–1.70$ g/cm^3 PVC-U: $\rho = 1.32–1.58$ g/cm^3
Colour	Any colour.
Transparency	Transparent, bluish.
Refractive index	PVC-U $n = 1.54$
Odour	Plastic smell, “new car” smell.
Usage	PVC-U – toys, pipes, window frames, credit cards. PVC-P – vinyl table coverings, films, inflatables, raincoats, artificial leather, hoses, cable insulation.
Pros	• Desired properties and plasticity can be achieved by various additives. • Good chemical resistance (especially PVC-U). • Good resistance to weather conditions. • Good insulation properties. • Does not ignite (high chlorine content). • Waterproof.
Cons	• Not very heat resistant. • Chemically unstable – additives dissipate from the polymerised mass over time. • Hard to produce (heat-sensitive).
Ageing	• Additives and ingredients migrate – HCl and phthalates are given off and can damage nearby objects. Plasticiser loss leads to contraction and stickiness, HCl accelerates ageing. • **Malignant plastic!** (damages other museum pieces).

Preservation	• Keep separated from other museum items. • Plasticised PVC must not be wrapped in absorbent materials (this facilitates plasticiser migration). • RH 35–40%, temperature < 16 °C.

History

Although PVC entered industrial use in the early 1930s, it was discovered much earlier. The monomer of vinyl was first successfully synthesised in 1835 by the French chemist Henri Victor Regnault, who treated ethylene dichloride with potassium hydroxide.[87] He obtained a white solid substance formed through gas-phase photopolymerisation. The discovery generated excitement but was confined to laboratories for many decades. Only in 1912 did the Russian chemist Ivan Ostromyslensky patent a PVC manufacturing process.[88]

In 1926, an American chemist, Waldo Semon, took an important step in the developmental history of PVC. The company BF Goodrich hired Semon to look for a synthetic substitute for natural rubber, which was becoming increasingly expensive and scarce. Semon's research led him to vinyl chloride, which proved easy enough to produce at the commercial level. Despite the Great Depression in the late 1920s, Semon was able to push through acceptance for the new material, proposing PVC-coated waterproof textiles. The new sales article quickly gained popularity.[89] In 1933, Semon developed the plasticised PVC we know today.[90]

Products

PVC saw continuous use during the Second World War, when it became a substitute for natural rubber as cable insulation. The high chlorine content (up to 57%) made them non-flammable, resistant to oil and water and – most importantly – non-reactive with copper wire.

There are two types of PVC: unplasticised polyvinyl chloride, PVC-U, which became popular in the 1960s, and plasticised polyvinyl chloride, PVC-P. PVC-U can withstand chemical and biological agents, which makes it a good choice for replacing corroded metal pipes (the first PVC plumbing system was installed in Germany in 1937). PVC-U can be used to make plastic window frames. Phonograph records are another well-known PVC product, introduced in 1948.[91] Plasticisers lower the polymer's glass transition temperature, keeping PVC-P elastic at room temperature. It is used to make hoses, cables, toys and inflatable objects.

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[87] Brydson 1999 [1966]: 298.

[88] Shashoua 2008: 28.

[89] History – PVC.

[90] Shashoua 2008: 28.

[91] The Plastics Historical Society, History & Development of the Vinyl LP Record.

Polyvinyl chloride (PVC) can be used in a wide range of products. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

Faux leather coat, 1970s. This trendy garment was made of PVC-P. ERM A 913:172/1–2

In 1940, the first vinyl textiles hit stores, which enjoyed a brief period of popularity as shower curtains at the end of that decade. In 1951, production collapsed due to lack of demand. The problem lay in the quality of the product – the patterns printed on the material quickly peeled off. They also gave off an unpleasant smell and became stiff after several months of use. The improvements to production technology naturally enhanced the quality of the product, but consumers' opinions of vinyl textile were far from positive.[92] Faux leather made of PVC-P saved its reputation – it became popular very quickly. It has seen widespread use from the second half of the 1950s to the present day. PVC leather withstands the elements and wear, making it a good choice for saddles on vehicles or boat seats. It is naturally also used a great deal for interior furniture, particularly in public eateries. Compared to polyurethane, it is more water repellent, firmer and less "breathable". PVC leather is thus mainly used in the fashion industry for raincoats, bags, belts and shoes.

Soft toys made by Polümeer factory, 1990. Photograph: A. Truuväärt. EFA.204.0-256775

Kid's inflatable chair, made of PVC at Polümeer in Tallinn. Photograph: E. Tarkpea, 1978. EFA.204.0-98777

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[92] Wahlberg 1994: 17.

2.2.7. Polyethylene

Abbreviation	PE (HDPE, LDPE)
Category	Thermoplastic
Discovered by	LDPE: 1937 – E.W. Fawcett and R.O. Gibson at I.C.I. (Imperial Chemical Industries), UK. HDPE: 1953 – Karl Ziegler, Germany.
Derived from	Polymerisation of ethylene (a gas). Currently derived from oil and natural gas, originally made from sugar cane.
Production	Low density polyethylene – LDPE (1940s, UK), high density polyethylene – HDPE (1953). The most widely produced plastic in the world.
Examples of product names	Stamylan, Lupolen, Vestolen, Alkathene, Eltex, Carlona, Marlex (USA), Ethafoam, Tyvek, Ethylux, Plastazote, Tenite (LDPE, USA).
Production methods	Injection moulding, extrusion, rotational moulding, thermoforming.
Solvents	Chloroform, nitric acid (70%), toluene, xylene, turpentine.
Glass transition temperature	LDPE/HDPE: $T_g = -65–125$ °C
Melting point	LDPE: $T_m = 110–120$ °C HDPE: $T_m = 130–137$ °C
Rigidity	LDPE – elastic, waxy. HDPE – fairly rigid and brittle. Both have soft surfaces that can be scratched with a fingernail.
Density	LDPE: $\rho = 0.915–0.935$ g/cm^3 HDPE: $\rho = 0.941–0.967$ g/cm^3
Colour	Milky, can be tinted any colour.
Transparency	LDPE – fairly transparent HDPE – cloudier
Refractive index	LDPE: $n = 1.51$ HDPE: $n = 1.54$
Odour	Reminiscent of paraffin.
Usage	Originally an insulating material for electrical wire and radar stations. HDPE is used to produce bottle caps, bottles (for non-carbonated beverages) and food containers, chemical-resistant pipe systems and chemical bottles, and sports equipment. LDPE is the main material for manufacturing plastic films.
Pros	• Good resistance to chemicals. • Inert. • Simple and inexpensive to produce.
Cons	• Does not tolerate higher temperatures. • Soft surface. • Low gas barrier. • Sensitive to UV radiation. • Absorbent material.
Ageing	• Photo-oxidation – yellows.
Preservation	• Avoid direct sunlight. • RH 35–45%, temperature < 23 °C.

History

In the early 1930s, an explosion occurred at the I.C.I. (Imperial Chemical Industries) laboratory in the UK – scientists had subjected ethylene gas to too much pressure. They had accidentally discovered polyethylene, the polymer with the simplest molecular structure. It would be several years before a use was found for the new plastic, and again it had to do with the military. In 1940, British engineers found that polyethylene was a superb insulator. Being lightweight as well, it was perfect for insulating portable radar stations. On-board radar systems on aircraft gave the RAF an edge over the Germans. The Royal Navy also introduced PE-insulated radar systems on board ships.[93]

Products

After the war, polyethylene became a fixture in consumer goods and the packaging industry. It was well suited for packaging body care and cosmetics products, and bottles containing household cleaners. It was also turned into lightweight, waterproof toys, and the little plastic skis many Estonians remember from their childhood. Bottle caps, seals, little boxes – polyethylene was suitable for all of these. In foamed form, polyethylene could be transformed into Ethafoam, which was inert and also a good insulator – it found use as a packaging material, pool flotation devices and conservation material for bolstering objects. And thanks to an enterprising American inventor and businessman named Earl Tupper, who developed airtight food storage containers called Tupperware, they have been used for refrigerated storage since 1947.[94]

The most widespread product made of polyethylene was introduced in the early 1960s. Swedish engineer Sten Gustaf Thulin developed a process that allowed a local plastics manufacturer, Celloplast, to produce a simple and durable plastic carrier bag. A film sleeve was spread flat, its bottom edge sealed by melting, and a section cut from the top to form handles — resulting in the now-familiar T-shirt-style carrier bag found in supermarkets worldwide.[95] Today, with plastic bags posing threats to marine life and caught in tree branches, it seems paradoxical that they were once supposed to reduce logging of forests. The inventor of the plastic bag, Sten Gustav Thulin, meant them to be re-usable as a substitute for paper bags.

In Estonia, polyethylene film began to be produced in the early 1970s at Tartu Kammivabrik (Tartu Comb Factory), which in 1972 was renamed Tartu Plastmasstoodete Katsetehas (Tartu Plastics Test Factory, TPK). Initially, plastic film was manufactured for agricultural purposes. In connection with the 1980 Moscow Summer Games, TPK was awarded a major contract to produce promotional plastic bags for the upcoming event. This was the start of plastic bag production that continues to the present day at Estiko-Plastar, as TPK has been called since 1991.[96]

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[93] Tradish 2004: 27–35.

[94] Hageman Collection, The History of the Product.

[95] Laskow, How the Plastic Bag Became So Popular.

[96] Kiiler 2004.

Promotional plastic bags for the 1980 Olympics (manufactured at Tartu Plastmasstoodete Katsetehas, a plastic factory in Tartu). Photographs: Estonian National Museum photographers. ERM A 983:7, ERM A 983:46

Polyethylene can be rigid or elastic, hard or soft. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

2.2.8. Polyurethane

Abbreviation	PU, PUR
Category	Thermoplastic, can also be a thermoset and elastomer.
Discovered by	1937 – Otto Bayer, Germany.
Derived from	Reaction between a diisocyanate (reactive compounds characterised by two NCO groups, e.g. toluene diisocyanate (TDI), polymeric polyisocyanate (PMDI) and polyol (low-molecular-weight alcohols – polyesters and polyethers).
Production	1937 fibres (Germany), 1940s varnishes/glues, 1949 rubbers; 1952 soft foam (USA, PU-ester), 1957 – polyurethane ether (USA), 1958 stretchy fibre (Lycra).
Examples of product names	Perlon U (Germany, 1940s), Porolon (foam), Lycra (fibre), Elastane (fibre), Spandex (fibre), Adiprene (elastomer), Vulkollan (elastomer).
Production methods	Reaction-injection moulding, calendering.
Solvents	Alcohols and ketones.
Rigidity	Rigid or elastic, high impact strength, scratch-resistant.
Colour	Any colour.
Usage	Varnishes, glues, foams, components that must tolerate high loads, artificial leather, rubbers, fibre.
Pros	• Remarkable versatility – can be produced with many different qualities and compositions (rubber, glues, varnishes, rigid materials, foams). • Substitute for natural rubber and leather. • PU leather and textiles are breathable materials.
Cons	• Does not tolerate higher temperatures, flammable (addition of flame retardants required). • Sensitive to oxygen. • PUR-ester is sensitive to moisture. • PUR-ether is photosensitive.
Ageing	• PUR-ether foams – oxidation (cross-linking of polymer chains). • PUR-ester foams – hydrolysis (scission of polymer bonds). • Photo-oxidation. • **Malignant plastic!** – as it ages, it gives off nitrogen compounds. If sticky due to hydrolysis, polyurethane ester can adhere to other items and damage them.
Preservation	• To prevent hydrolysis, PUR esters must be stored in dry conditions (RH 35–45%). • PUR ethers are degraded by UV light, so they should be kept away from direct and indirect sunlight. Even visible light damages the material. The time on display should be brief. • RH 35–45%, temperature < 18 °C.

History

In the 1930s, I.G. Farben Laboratories in the German city of Leverkusen attempted to develop new synthetic materials to supplement its chemical product range. In 1937, Dr. Otto Bayer succeeded in developing the diisocyanate polyaddition process. His discovery paved the way for a new polymer – polyurethane.[97]

Its simple manufacturing process and versatility meant polyurethane quickly gained numerous uses. Since it was a polymer that was resistant to chemicals, to the elements, and to mechanical wear, it was initially used as a varnish for protecting metal, wood and masonry. Polyurethane was also used for treating fabrics to make them resistant to Iprite (mustard gas).[98]

Products

Interestingly, polyurethane is a misnomer, as it does not consist of urethane monomers. Even stranger, their macromolecules do not even contain urethane groups.[99] Instead, they are produced by the reaction of diisocyanate with polyol. Diisocyanates are highly reactive compounds. Flexible polyurethane foam is primarily made from toluene diisocyanate (TDI). Polymeric methylene diphenyl diisocyanate (PMDI) can also be used. Polyols are low-molecular-weight alcohols that react with the diisocyanate to form the polymer network.

Initially, polyester polyols were used; later, polyether polyols were also developed. Which of these polyols is used, determines the chemical and physical properties of the polyurethane. Polyurethane ethers are resistant to weathering, while polyurethane esters have superior mechanical properties and show greater tolerance to oils and solvents.[100]

Thermoplastic elastomers can easily be formed to produce automotive components (from the 1980s), ski boots, roller skate wheels or electrical insulation. They can also be drawn into elastic filaments. Fibre is known as Spandex (marketed under trade names such as Lycra and Elastane), and sportswear made from these materials first appeared in 1958.

Swimsuit made of elastane, 1990s. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

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[97] Sharmin, Zafar 2012.

[98] How Products Are Made, Polyurethane.

[99] Rubin 1990: 511.

[100] Sharmin, Zafar 2012.

A very good substitute for leather can also be produced from polyurethane, a good deal softer and more permeable than real leather and suitable for making skirts, trousers and jackets.[101] However, since 1950 it has been used most widely as polyurethane foams, which can be rigid, semi-rigid or flexible (foam rubber). Rigid foams are used for building insulation (PUR insulation) and furniture, semi-rigid foams are for car interiors, while soft foams are used in the furniture industry.

Faux leather made of polyurethane can be a convincing imitation of the genuine article. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

Examples of polyurethane foam. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

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[101] Keneghan, Plastics Making a Splash!

2.2.9. Polypropylene

Abbreviation	PP
Category	Thermoplastic
Discovered by	1953 – Karl Ziegler (Germany) and Giulio Natta (Italy).
Derived from	Polymerisation of propylene monomer in the presence of Ziegler-Natta catalysts. Derived from petroleum.
Production	Started in the 1950s, popular in the car industry from the 1970s. Worldwide production volume is the second highest of any plastic.
Examples of product names	Marlex (USA), Tenite (USA), Luparen, Propathene, Moplen.
Production methods	Injection moulding, extrusion, vacuum forming.
Solvents	Chloroform, nitric acid (70%), toluene, xylene, turpentine.
Glass transition temperature	(atactic) Tg = −20 °C (isotactic) Tg = 0 °C
Melting point	Tm = 176 °C
Rigidity	Rigid yet elastic, can be bent repeatedly.
Density	$\rho = 0.9\ g/cm^3$
Colour	Any colour.
Transparency	Fairly transparent.
Refractive index	n = 1.49
Odour	Reminiscent of paraffin.
Usage	Textile fibres, sheets of film, consumer goods, toys, drinking straws, ropes, chair frames, canisters, food storage containers, rugs.
Pros	• Good mechanical and dielectric properties. • Good resistance to high temperatures. • Easy to shape. Very good chemical resistance. • Very good resistance to repeated bending. • The lightest plastic in terms of weight.
Cons	• Flammable. • Fragile in cool temperatures. • Low resistance to UV radiation.
Ageing	• Becomes brittle in the cold. • Photo-oxidation.
Preservation	• Avoid direct sunlight. • RH 35–45%, temperature < 23 °C.

History

In 1957, a transparent plastic film and durable filaments were demonstrated in Italy, made of yet another new plastic – polypropylene. It was discovered by two chemists working independently of each other. In 1953, German chemistry professor Karl Ziegler discovered that certain metal compounds can be used as catalysts for polymerisation reactions. This knowledge was used the same year by the Italian chemist Giulio Natta for the chain polymerisation of propene. The result was isotactic polypropylene, which was very similar to HDPE.[102] The differences were that the new polymer had a higher softening temperature, rigidity and hardness. But brittleness due to its high molecular mass made it nearly impossible to produce items from it. Molecular mass was kept under control by adding hydrogen to the polymerisation reaction. In the mid-1980s, polypropylene became the third most widely produced plastic in the world. Today, polypropylene is the second most produced plastic.[103]

Products

Polypropylene's first widespread uses were as a textile fibre and thin transparent sheet film used to package bread products and other goods. In the early 1960s, it began to be used for pipes, cable insulators, and the bane of today's environmental conservationists – drinking straws. The production of plastic straws in the EU has been banned since July 2021.

Polypropylene's most significant property is its thin sections, which can withstand repeated bending. It therefore makes a suitable material for manufacturing boxes and containers in one piece with moulded hinges (e.g. Tic-Tac boxes). Polypropylene is used in the packaging, furniture, toy and textile industries (the fibres can be used for fabric and rugs). Since it does not absorb water, it is ideal for making rope for outdoor use. It can also be produced in sheet form, used for example as binder pouches and polymer banknotes.

Polymer banknotes are another interesting product, used in the UK, Romania, Australia, Canada, and New Zealand, for example.


Tic-Tac boxes are made of polypropylene. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

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[102] Brydson 1999: 240.
[103] Plastics Technology, No. 2 – Polypropylene.

Polypropylene items. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

2.2.10. Unsaturated polyester resin

Abbreviation	UP resin
Category	Thermoset
Discovered by	1933 – Carleton Ellis.
Derived from	Phthalic acid anhydride or isophthalic acid and maleic anhydride are reacted with dialcohol (diethylene glycol, propylene glycol).
Production	1941 USA. Wide commercial use starting in the 1950s.
Examples of product names	GRP, fiberglass, Polyplex, Synolite, Lamellon, Setarol, Leguval, Palatal.
Production methods	Casting.
Solvents	Concentrated acids, toluene, xylene, styrene, benzene, phenol.
Decomposition temperature	150 °C (extensive decomposition starts at 360 °C).
Rigidity	Rigid.
Colour	Any colour, transparent.
Transparency	Transparent.
Refractive index	n = 1.55
Usage	Binder for fibreglass (boats, furniture, swimming pools, enclosures); extensive use in art – cast sculptures, jewellery, and fibreglass-reinforced shapes; surfacing.
Pros	• Weather-proof. • Good mechanical properties. • Good bond with fibreglass. • Good resistance to corrosion.
Cons	• Rigid and brittle. • Flammable.
Ageing	• Photo-oxidation and hydrolysis, which leads to micro-cracks on the surface, fading and reduction of molecular mass (material becomes brittle).
Preservation	• Avoid direct sunlight and extended exposure to water. • RH 35–45%, temperature < 23 °C.

History

The patent for production of unsaturated polyester resin was issued in 1933 to the American chemist Carleton Ellis, who studied the possibilities of synthetic surface coatings. The development of commercial polyester resins started in American chemical laboratories in the 1940s. The first polymerisation reactions required heating, which made the process too complicated for widespread use of the new polymer. Polyester resin was used by defence manufacturers for producing reinforced fibreglass protective shells for radars. By 1946, cold cure polyester resins were developed, making it easier to use. After the war, use of polyester resin spread to consumer goods, including furniture, car, boat and construction industries.[104]

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[104] The Plastics Historical Society, Polyester Resin.

Products

As practically everyone these days has sat in a plastic chair, it may seem a little comical that the first ones were seen as abstract art. After the Second World War, the husband-and-wife architects Charles and Ray Eames researched the especially strong structural plastic for military aircraft – fibreglass reinforced polyester. This new material gave the designers free rein in terms of form, leading to the birth of moulded plastic dining chairs and armchairs on thin metal legs, that are now considered classics. On sale in America since the 1950s, these mass-produced chairs were the first furniture items where plastic had become a visible design component.[105] The Eames chairs were the genuine pioneers for other types of plastic furniture. In their footsteps were to follow designers such as Eero Saarinen from Finland with a tulip-shaped chair and Eero Aarnio with his "cognac chair", which the Estonian Consumers' Cooperative plant Kooperaator shamelessly plagiarised and started producing in 1974 as the P-30.[106]

Armchair P-20 by Kooperaator made of epoxy resin and here as an example of the copied design. Restoration work and photograph: Triin Kaasiku

The RAR rocking armchair; shell made of a polyester and fiberglass, 1948/1950, designed by Charles and Ray Eames. Photograph by the author. Pinakothek der Moderne, Munich

The furniture industry is only one of the many sectors that use unsaturated polyester resin. As it can be used as a binder for different materials and be reinforced with glass or carbon fibres, polyester resin is suitable for producing items including boat hulls, enclosures, wall panels, swimming pools and sports equipment. Nor, of course, were the possibilities of the material overlooked by sculptors. Even the fashion industry found polyester resin to be beneficial – many mannequins are made of glass reinforced polyester (GRP).[107]

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[105] Keneghan, The World of Charles and Ray Eames ...
[106] Paulus 2006.
[107] Christjanson 2007: 53.

2.2.11. Polyethylene terephthalate, polyester

Abbreviation	PET, PETE
Category	Thermoplastic
Discovered by	1940 – John Rex Whinfield and James Tennant Dickson, UK.
Derived from	Ethylene glycol (a colourless, odourless sweet-tasting but toxic syrup, antifreeze) is reacted with dimethyl terephthalate or terephthalic acid (both white solids). Derived from petroleum.
Production	PET film and fibre production started in the USA in the 1950s. Pellets for injection moulding were first produced in 1966 in England. Used for carbonated beverage bottles since 1970.
Examples of product names	Terylene (fibre), Dacron (fibre), Tergal (fibre), Mylar (film), Melinex (film), Arinite, Fluon, polyester (fibre).
Production methods	Extrusion, injection moulding.
Solvents	Acetone, concentrated acetic acid (> 30%), ammonia, benzene, chloroform, concentrated hydrochloric acid.
Glass transition temperature	Tg = 80 °C
Melting point	Tm = 254 °C
Rigidity	Rigid or elastic.
Density	$\rho = 1.40$ g/cm^3
Colour	Any colour.
Transparency	Transparent.
Refractive index	n = 1.55–1.64
Usage	Carbonated beverage bottles, textile fibres, polyester wadding, artificial hair, inert sheets of film, camera film and photographic negatives.
Pros	• Can be made into either amorphous or semi-crystalline plastic. • Very good transparency. • Easy to mould. • Good barrier properties (blocks oxygen and carbon dioxide) and water resistance. • Good resistance to solvents. • Easy to recycle.
Cons	• Light sensitive. • Shrinks as it solidifies (up to 12%).
Ageing	• Stable. • Yellows over time due to photo-oxidation.
Preservation	• Avoid direct sunlight. • RH 35–45%, temperature < 23 °C.

History

A close look at a soft drink bottle often reveals the acronym PET or PETE, signifying “polyethylene terephthalate”. The word polyester may be more familiar. This is a thermoplastic, a polycondensate of terephthalic acid and ethylene glycol. It was first produced in 1940 by two chemists at DuPont, J. Rex Whinfield and James T. Dickson. Commercial production of PET under the trade name Mylar began in the USA in 1951.[108] Initially, it was used for photographic negatives and film stock. Today, polyester film remains widely used in conservation, valued for being chemically inert and for its excellent long-term stability.

Products

PET is a good gas barrier and has low water absorbency. Thanks to its physical properties, DuPont engineer Nathaniel Wyeth got a patent for a plastic bottle for carbonated beverages in 1973. They were on American store shelves in 1977. Today nearly half of all soft drinks are packaged in plastic bottles.[109]

In addition to bottles, polyester has also been produced in fibre form since the 1960s for making textiles. When polyester clothes first hit stores, they were advertised as miracle fabric, they were immune to wrinkling and didn't need ironing. They dried fast and their colours and patterns remained bright for a long time. Today polyester is a common material for sportswear. Adding PET fibres to linen or cotton reduces wrinkling. Very fine fibres are used to make synthetic silk, while coarser ones are used for car tyres, conveyor belts and seat belts. It's worth mentioning that PET is the plastic that is easiest to recycle and a large part of the returnable plastic bottles are turned into fibre, so it's no joke to say that sportswear is made from soft drink bottles.

Soft drink bottles are made of polyethylene terephthalate. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

Costume made of polyester fabric, 1980s. TM E 223: 6 1–2

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[108] The Plastics Historical Society, Polyethylene terephthalate.
[109] How Products are Made, Soda Bottle.

2.2.12. Epoxy resin

Abbreviation	EP, EPO, GRE (glass reinforced epoxy)
Category	Thermoreactive, amorphous
Discovered by	1938 – Pierre Castan (Switzerland).
Derived from	The most common method is a reaction between bisphenol A and epichlorohydrin.
Production	From 1940, commercially since the late 1950s.
Examples of product names	Epicote, Araldite, Hxtal NYL-1, Fynebond, Aldebond, Rutapox, Epotek.
Production methods	Casting.
Solvents	Concentrated acids, solvents containing chlorine.
Decomposition temperature	230 °C
Rigidity	Rigid.
Density	$\rho = 1.25$ g/cm^3
Colour	Transparent, often slightly yellow (due to the activator).
Transparency	Transparent.
Refractive index	n = 1.52–1.57
Usage	Coatings, glues (better construction glues), plasters, castable objects, laminates and composites.
Pros	• Minimal shrinkage and internal tensions after curing. • Good chemical resistance to many solvents. • No toxic volatile organic compounds given off after solidification. • Weather-proof. • Stability in changing environmental conditions. • Very good adherence to different materials, including metals and glass.
Cons	• EPO is impossible to remove from porous surfaces as it does not dissolve completely in any solution (it merely swells, after which the glue must be mechanically removed from the surface). • May be brittle due to its rigidity. • Commercial EPO resins may contain compounds that result in rapid yellowing. • A defect may appear when mixing the two components, due to which the proper polymerisation reaction does not take place, leaving the result substandard. • More expensive than unsaturated polyester resin.
Ageing	• Yellows over time due to photo-oxidation and reactions between the components (in the dark). • The shorter the cure time, the faster it yellows.
Preservation	• Avoid direct sunlight. • RH 35–45%, temperature < 23 °C.

History

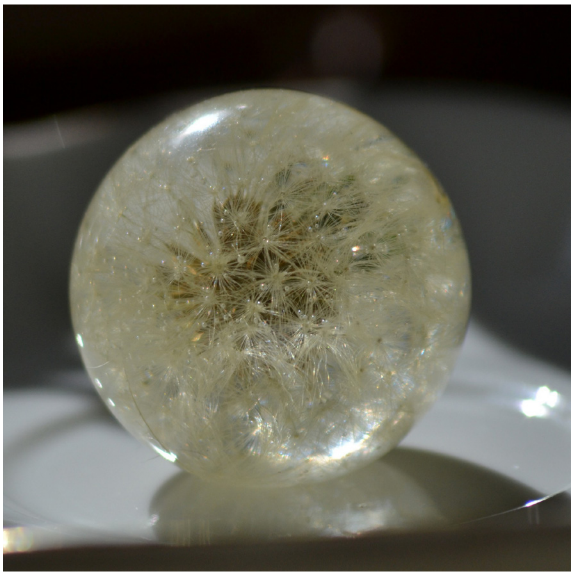
In 1936, a Swiss chemist, Dr. Pierre Castan, succeeded in creating an amber-coloured polymer that withstood higher temperatures and had noteworthy mechanical properties. For the new polymer, he reacted bisphenol A with epichlorohydrin. The result was the invention of epoxy resin. The first application was in dental fillings. Castan was awarded several more patents for different types of epoxy resins.[110]

As many different materials (fibreglass, textile, sawdust and veneer) could be used as filler in the resin to form strong load-bearing structures, the new polymer gained great popularity in the late 1950s. Epoxies are superb adhesives and can be used to fuse just about any material (other than oil and grease covered surfaces). Epoxy resin was also a durable surface coating.[111]

Products

Epoxy resins are mainly used as adhesives. It is widespread as an emulsion finish for protecting metal household appliances, the shipbuilding industry, the lining of metal jugs and tins of food (particularly tins of acidic foods). It has also expanded to various countertops, worktops, and flooring surfaces. Because epoxies shrink very little upon curing, they make good plasters and sealants. Reinforced with fibreglass, textiles or carbon fibre, they form strong load-bearing structures that have found a use in the furniture industry and for making various structures (such as recreational vehicles). Epoxy resin is also popular among jewellery artists, as it is a good medium for inserting insects, flowers or fish scales.[112]

Shimmering earrings by Sigrid Kuusk, cast from epoxy resin. Photograph by Sigrid Kuusk



Epoxy resin provides an attractive coating for various items and materials, such as jewellery. Jewellery design and photographs: Kristina Aas

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[110] The Plastics Historical Society, Pierre Castan.
[111] The Plastics Historical Society, Pierre Castan.
[112] Negoita, Cristache, Bodor 2016.

2.2.13. Polycarbonate

Abbreviation	PC
Category	Thermoplastic
Discovered by	1953 – Hermann Schnell (Germany) and Daniel Fox (USA).
Derived from	Reaction between bisphenol A (product of phenol and acetone) and phosgene (a colourless gas that breaks down into hydrochloric acid in the body and leads to death by asphyxiation).
Production	First produced as sheets of film for photographic negatives and electronics, and then as various impact-resistant items and “glass” (1959, Germany; 1960, USA).
Examples of product names	Lexan (USA), Makrolon (USA), Calibre (USA).
Production methods	Extrusion, injection moulding, rotational moulding, casting.
Solvents and Reactants	Acetone, benzene, chloroform, formic acid, nitric acid (70%), potassium hydroxide (50%), sodium hydroxide (50%), toluene, xylene, turpentine.
Glass transition temperature	T_g = 145–150 °C
Melting point	T_m = 230 °C
Rigidity	Rigid, but more elastic than PMMA.
Density	$\rho = 1.2\ g/cm^3$
Colour	Any colour.
Transparency	Transparent.
Refractive index	n = 1.59
Usage	Transparent or coloured reusable water bottles and tableware, car headlights, eyewear, helmet visors, bus stop shelter walls, awnings.
Pros	• Very good mechanical resistance to wear and impacts. • Excellent transparency.
Cons	• Vulnerable to many solvents. • Vulnerable to UV radiation.
Ageing	• Photo-oxidation – the material yellows over time.
Preservation	• Avoid direct sunlight. • RH 35–45%, temperature < 23 °C.

History

1958 saw the introduction of a strong, rigid, heat-resistant, chemically stable and extremely transparent plastic – polycarbonate. In 1953, the plastic was simultaneously developed by two scientists working independently of each other – a German, Hermann Schnell at Bayer and the American Daniel Fox at General Electric. The Germans patented the new material as Makrolon, while the Americans called it Lexan. Polycarbonates are polyesters of carbonic acid, made by reacting bisphenol A and phosgene ($COCl2$)[113].

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[113] The Plastics Historical Society, Polycarbonate.

Products

Polycarbonate is very resistant to impacts (does not break into shards if damaged) and has superb transparency. Thanks to these properties, the plastic is widely used in impact-resistant protective gear, safety goggles, windscreens, bus stop shelter roofs, awnings, lamp covers on traffic lights, gym windows, kitchen equipment utensils and appliances, microwave-safe food containers and reusable drink and baby bottles.[114] Since 1982, polycarbonate has been used for CDs. In the 1990s, thanks to its optical properties and its light weight, polycarbonate began to be used for both safety goggles and prescription glasses. In 1994, the first car with polycarbonate headlights was brought to the European market, the Opel Omega.[115]

A polycarbonate “glass”. Photograph: Anu Ansu and Berta Jänes

CDs are made of polycarbonate. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

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[114] Lippmaa 2001: 222.

[115] Bayer, History of Polycarbonate at Bayer.

3.

IDENTIFYING PLASTICS

If you see the word “plastic” describing an item, it simply means that it is made of a substance that can be moulded and shaped under heat and pressure. A “plastic” can be natural or man-made. It may be semi-synthetic or completely synthetic. It can be a thermoplastic, vulnerable to solvents and high temperatures, or a more durable thermoset. Some plastics are malignant, meaning that as they degrade they also damage nearby objects, and others are inert and benign. The word “plastic” brings up a number of questions that are extremely important for the successful storage and conservation of a plastic item.

Most natural materials can be stored under quite similar conditions. Taking wood as an example, there is no particular difference as to whether it is oak, pine or birch; similarly, there is no fundamental distinction between goat, sheep and cow hide. But plastics are different. Although all plastics should be kept in a dark, cool and well-ventilated space, the required level of relative humidity varies, as are the kinds of materials they can be stored with.

Besides the differences in storage conditions, determining the type of plastic is important when it comes to practical conservation. The glues, solvents, cleaning agents, reinforcers and fillers that are used, are dependent on what the item is made of. If the plastic in an object cannot be identified, all chemical intervention for the purpose of conservation should be forgone. Even damp-wiping an object with clean water could cause irreversible damage to an item made of, for example, aged Galalith or nitrocellulose.

Sometimes merely knowing the history of the product’s design and when a given plastic was introduced allows us to date a plastic without technical equipment. The tables in this book’s appendices are a useful resource: one table provides information on when plastics were introduced while another contains information on the local (Estonian) development of plastics.

Laboratory analysis is however the most accurate way of identifying plastics. The analytical method most widely used is Fourier transform infrared spectroscopy (FTIR). The result obtained is a spectrum, which is then compared with other spectra in a database to identify the plastic under consideration. UV spectroscopy can help to determine additives in a plastic. Metals contained in a compound are found by means of atomic absorption spectroscopy (AAS). X-ray fluorescence spectroscopy (XRF) reveals the presence of inorganic fillers and pigments. Raman spectroscopy determines the polymer types and impurities in their composition. Gas chromatography-mass spectrometry (GC-MS) is effective for finding trace components.[116] Admittedly, many conservators, to say nothing of collectors, lack access to sophisticated apparatuses. Consequently, this chapter will focus on more basic methods for distinguishing plastics. The final identification of material must be made based on numerous criteria.

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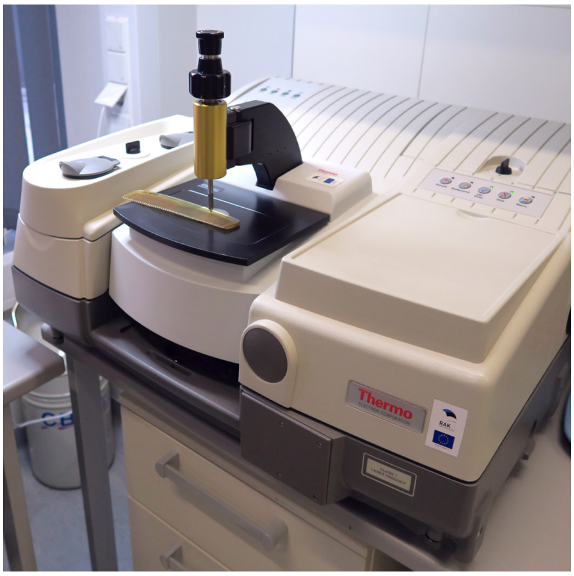
116 Forrest 2002.



Infrared spectroscopy analysis device. In the picture, the material of a comb is being identified. Photograph by the author

To compare the test results, the spectrum obtained from FTIR analysis is compared to spectra in a database. This requires experience and a large set of data. Photograph by the author

Everything possible should be considered: history, production technology, the properties of the material and the purpose for which the item was used. The identification attempt should be made without damaging the item. However, if questions remain and the material has to be identified quickly, then the use of less safe methods could be considered.

3.1. Non-destructive identification methods

We have before us two white mugs. One is slightly larger than the other and their handles have differing designs, but otherwise they are quite similar. Picking up the mugs, we recognise that one is ceramic and the other is plastic. Lesson 1 – looks can be deceiving! Especially so for plastics, which were created in the first place to imitate natural materials.

Two ostensibly similar mugs. The left one is ceramic, the right one is plastic. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

The mug on the right turned out to be plastic. Let’s take a closer look:

- it has a glossy surface;
- its surface is hard and it cannot be scratched with a fingernail;
- it is lightweight;
- it sounds metallic when tapped;
- it is translucent when held up against the light;
- it is a mass-produced product, so it must be made of a cheaper commodity plastic:
- a circular impression at the mouth of the injection moulding channel (sprue) can be seen, a sign that it is a thermoplastic;
- looking at the bottom of the mug, we see three markings: “MADE IN CHINA”; a symbol depicting a glass and a fork, which means that the item is food-grade, and a triangle composed of three arrows with the number 6 in the centre and the letter combination “PS” below it.

Information on the bottom of a mug about the material. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

The last of these gives us a definitive answer for identifying the material. It is polystyrene. We were fortunate. In the absence of the recycling symbol that refers to polystyrene imprinted on the bottom, our decision-making tree would have been the following:

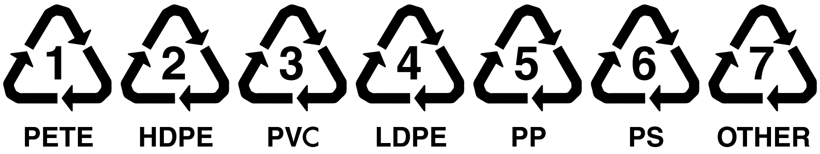
1. Consumer plastic, thermoplastic – PE, PP, PS, PVC, PMMA, PC?
2. Glossy, hard surface – PS, PVC, PMMA, PC?
3. Food-grade – PS, PMMA, PC?
4. Sounds metallic when tapped – PS!

As this example shows, background knowledge is very important for identifying a plastic by its appearance. For example, PVC is not used for tableware. The fact that the item is lightweight, lets some light through and is thermally moulded, rules out melamine formaldehyde, which is used for making similarly glossy tableware. It should also be considered that polycarbonate is the most expensive of the three remaining options. Even though all three are amorphous and thereby translucent, there would be no point in tinting expensive polycarbonate with pigment, given that ideal transparency is one of its special features.

In the next section, we look at the properties of the materials and tips for identifying plastic material without damaging it in the process.

3.1.1. Recycling system symbols

In 1988, the USA introduced a plastics recycling system that helps in sorting plastic materials for reuse. The logos are composed of arrows moving clockwise in a triangle. In the centre is a number from 1–7 and underneath is the abbreviation of the name of the plastic. The symbol is generally in an inconspicuous location, such as the bottom of the item. The number indicates the ease of recycling. Polyethylene terephthalate (PETE, PET) is the easiest to recycle and is indicated by the number “1”. The number “7” found on an item can indicate polycarbonate, nylon, acrylic or a copolymer.



The following information can also be found about the plastic:

- 100% melamine – melamine formaldehyde.
- BPA-FREE – polycarbonate, made not from bisphenol A but some other bisphenol.
- Tritan – a very durable BPA-free copolyester; a substitute for polycarbonate

A cup made of melamine formaldehyde. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

Information on the bottom of a cup

3.1.2. Transparency

If the item is transparent, the plastic that was used to manufacture it may be:

- **Polycarbonate (PC).** The item is meant to tolerate impacts, scratches and temperatures up to 100 °C. Expensive material.
- **Polymethyl methacrylate (PMMA).** The item is ideally transparent but does not withstand harder impacts and scratches easily.
- **Polystyrene (PS).** The consumer plastic that is most widely used for transparent items. Not very strong and elastic. Glass transition temperature around 80 °C.
- **Polyethylene terephthalate (PET).** Transparent bottles for carbonated beverages, packaging.

Polycarbonate drink bottle. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

Utensils made of PMMA. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

Transparent packaging and bottles for cosmetics are mostly made of polyethylene terephthalate. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

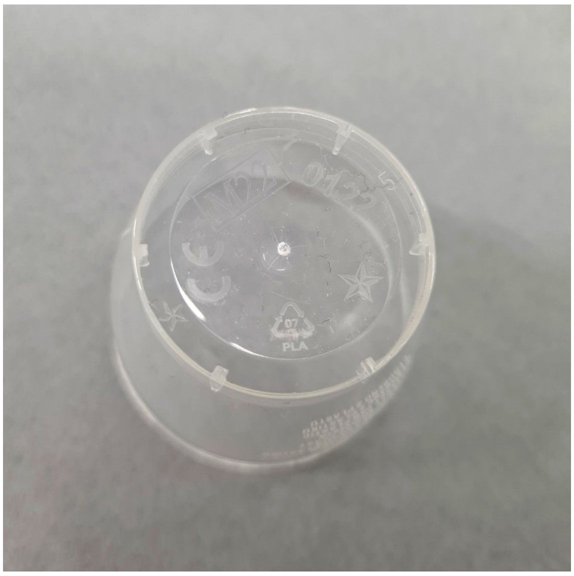
Soft drink bottles are made of polyethylene terephthalate. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

- **Styrene-acrylonitrile resin copolymer (SAN).** This plastic is used when the item must withstand a higher temperature, be impact-proof and resistant to chemicals. The last of these properties is the primary one and distinguishes SAN from PC. Plastic cups are an example – polycarbonate shows signs of wear after about 100 dishwasher cycles while SAN keeps looking good up to 1000 cycles. Yet PC is more impact resistant.
- **Polypropylene (PP).** Slightly cloudy, relatively soft surface that scratches easily.
- Small cast items (like jewellery) may be made of epoxy **resin (EP).** Quite heavy compared to thermoplastics.
- Polylactide (PLA). Mainly for single-use containers and packaging. Has a yellowish undertone. In terms of perceived quality, between PET and PS.
- If the item is older, a tinted transparent material may be Bakelite (without filler) or **Catalin** (introduced in 1928).

Container made of styrene acrylonitrile resin. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

Thinner polypropylene items can be fairly transparent. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

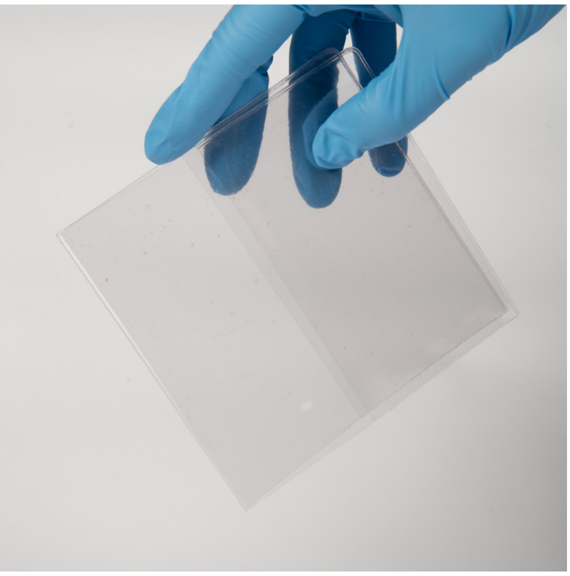
A flower encased in epoxy resin. Jewellery design and photograph: Kristina Aas



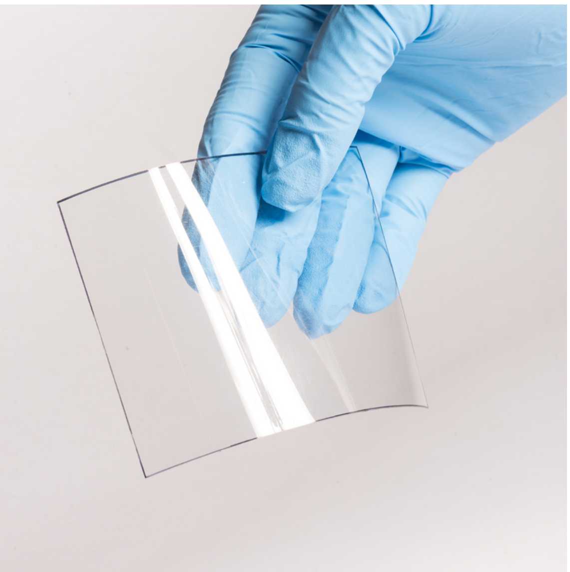
Single-use drinking cup made from polylactide, with the abbreviation PLA visible on the bottom. Photograph by the author

A transparent film sheet may be made of the following plastics:

- **Plasticised polyvinyl chloride (PVC-P).** Glossy, elastic, rubbery, cross-section bluish in tone.
- **Polyethylene terephthalate (PET).** Glossy, very durable films, thinner sheets of film crinkle like cellophane.
- **Polypropylene (PP).** Can be matte or glossy, cloudy or transparent.
- **Polyethylene.** High-density polyethylene (HDPE) is significantly cloudier and crinkles when crumpled more than low-density polyethylene (LDPE).
- **Nitrocellulose (NC)** or **cellulose acetate (CA).** Older films (photo negatives, film strips); often turn yellow.
- **Cellophane.** Regenerated cellulose; a thin, crinkling sheet of film used in the food industry and for gift wrapping.

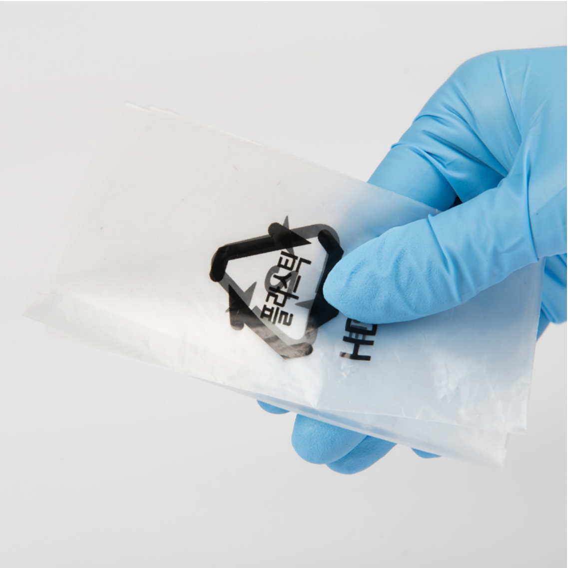


A freshly manufactured plasticised PVC (PVC-P) sleeve. PVC-P often has a bluish tone, but with the passage of time, is fairly quick to turn yellow. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples



Melinex polyester film. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

A plastic sleeve made of polypropylene. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples



A high-density polyethylene film is considerably cloudier than a low-density polyethylene film. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

Cellophane is a highly transparent, crinkly film that is often used for gift wrapping as well as for wrapping cigarette and tobacco packages. This is because cellophane allows water vapour to pass through, which is an important property for packaging tobacco products. Photograph by the author

Good to know: transparent items are generally not produced from the following plastics:

- acrylonitrile butadiene styrene (ABS);
- polyamide (nylon, PA)
- melamine and urea formaldehyde (MF, UF);
- Bakelite (phenol formaldehyde with a filler);
- casein formaldehyde.

3.1.3. Hardness and elasticity

The hardness of a plastic can be altered by plasticisers and hardeners. For example, PVC is used to produce hard, durable water pipes and stretchable waterproof boots and raincoats. For that reason, the surface hardness of plastic can sometimes be misleading. Still, a few rules of thumb:

- Polyethylene and polypropylene are “waxy” plastics. They can be scratched with a fingernail. Polypropylene is harder and glossier.
- Polystyrene always has a hard surface (unless it is foam). Higher impact items are made from high impact polystyrene (HIPS).
- Thermosets tend to be more brittle. The fillers also make them heavier. Therefore Bakelite, urea and melamine formaldehyde objects are always hard and heavier than polypropylene, for example.
- Acrylonitrile-butadiene-styrene (ABS) is hard but elastic enough to withstand hard impact.
- To tell the difference between sheet polycarbonate (PC) and polymethyl methacrylate (PMMA), remember that PC is more elastic. When bent on the corner of a tabletop, PMMA will snap in two, while PC will initially bend. PMMA will have cracks radiating out from the break, but PC does not exhibit this pattern.

Plastics used for manufacturing both rigid and elastic materials:

- Polyurethane (PU). Used to produce structural parts subjected to heavy loads and also elastic artificial leather, foam plastic and stretchy fibres.
- Polyvinyl chloride (PVC). Plastic window frames, inflatable swimming rings and bath toys.
- Polyamide (PA). Durable structural parts and also stretchy stockings.
- Natural rubber (NR). “Rubber” items as well as objects of vulcanised rubber (ebonite).

3.1.4. Odour

Sometimes, plastics can even be identified by odour. The older the plastic, the more of a characteristic smell it gives off. And as always with chemicals, the warmer a material is, the more pronounced the odour is. In order to bring out the smell, an object can be rubbed with a soft piece of cloth (caution: rubbing can cause micro-scratches on the surface) or dipped in hot water for a second (don't use this technique on museum pieces because water can damage plastic). Odours become especially prominent when an item is subjected to a burn test, discussed in the next chapter.

- Nitrocellulose – camphor, reminiscent of pine resin
- Cellulose acetate – vinegar smell
- PVC-P – pastel crayons
- Phenol formaldehyde – antiseptic
- Polyethylene and polypropylene – candle, plastic bag smell
- Natural rubber – sulphur, “rubber smell”

3.1.5. Signs of age-related degradation

The only upside of degradation for a conservator is when it aids in identification. Several plastics have distinctive ageing characteristics.

A powdery residue coating an object that can be wiped off easily may be an additive that has migrated to the surface. This is seen in the case of nitrocellulose, cellulose acetate and PVC-P. In the world of conservation, this is known as “blooming”.

The plasticizers in PVC have migrated to the surface over time, forming a white powdery coating. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

If an item is cracked all the way through, as a result of which it looks like broken tempered glass, it may be nitrocellulose.

If the object is elastic and its surface has become oily and sticky, it is probably plasticised PVC that is experiencing plasticiser migration to the surface.

Heavily aged nitrocellulose. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

Plasticised PVC that has become sticky. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

If the object is made of stretchy expanded plastic and has become very brittle and “dry”, it is polyurethane ether or natural foam rubber. If an expanded plastic object has become sticky and has deflated, it may be polyurethane ester.

Aged polyurethane ester foam becomes sticky and collapses under its own weight. Photograph: Anu Ansu and Berta Jänes. ERM A 826:153

Oxidation turns foam rubber hard and very brittle over time. Photograph: Anu Ansu and Berta Jänes. ERM A 826:272

3.1.6. Special characteristics

Sometimes people ask me, “Well, what kind of plastic is this?”, figuring they have something that is sure to stump me. I spoil the fun with a quick utterance: “polypropylene!“ Indeed, there are a number of plastics that have peculiarities, due to which certain items are made only of that plastic. There may be a few exceptions, but most of the following statements hold true:

- If an object with a hinge or a snap fastener was cast as a single piece, it is usually made of polypropylene. This plastic’s special power is that it can withstand repeated bending. An example of this is the lid on a box of Tic-Tacs, which is a clue that it is polypropylene.
- When Earl Tupper started making his food storage containers in the early 1950s, he used polyethylene. Containers were made from this plastic for decades. This continued until microwaves became popular in households and in one movement, stored food with the container was placed directly from the fridge into the oven. It was quickly discovered that polyethylene softened and deformed when heated. Because of this, Tupperware containers began to be made from heat-tolerant polypropylene. These containers have the inscription “Microwaveable” or the abbreviation PP on the bottom.
- Polypropylene, however, does not withstand freezing. It becomes quite fragile at 0 °C. Sleds and plastic skis are therefore made of polyethylene, even though polypropylene resists wear better than polyethylene.
- The elastic legs and heads of Barbie dolls are made of plasticised PVC.
- Until 2014, table tennis balls were made only of nitrocellulose (starting from 1901). The primary material used today is ABS.
- Lego bricks are made from ABS, as are many other premium toys, such as Transformers and other action figures. Cheaper toys with a hard surface that make a specific resonant sound when tapped on are pure PS plastic.

3.2. Destructive identification methods

With sufficient experience, plastics can be identified without damaging the item. But if a positive identification cannot be made, more damaging identification methods have to be used. In the case of items in museum collections, it should be considered whether and to what extent the object’s integrity can be compromised. The attempts described require a fairly large sample piece, and such a sacrifice can’t come at the expense of a unique museum piece.

3.2.1. Burn test

Heating a sample of the material allows us to determine whether it is a thermoplastic or thermoset. In a burn test, the sample is allowed to catch fire in a flame. We examine how fast the plastic ignites, the nature of the flame, the amount and colour of the soot, the odour and the appearance of the burnt area. The test must be carried out under a ventilation hood, because a number of plastics (especially PVC and PS) give off very toxic substances. Thermoplastics ignite easily. Thermosets, on the other hand, char and do not ignite. It is worth noting that PVC tends to self-extinguish shortly after removal from the flame because of its high chlorine content. So does cellulose acetate. Polyethylene and polypropylene burn with a slower, bluish flame, reminiscent of a candle flame, giving off white smoke with a paraffin-like odour. On the other hand, polystyrene burns with an intense, sooty flame.

To better interpret the results of the burn test, the appendices include an illustrative table on the combustion of various plastics (see Appendix 5. Identifying plastics with the burn test, page 191).

3.2.2. Solubility test

A solubility test is somewhat easier to interpret than a burn test. Bear in mind that thermosets are more resistant to solvents than thermoplastics.

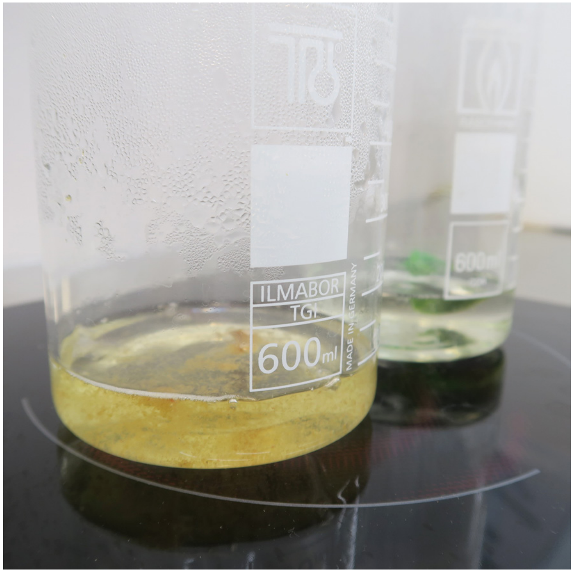
To carry out the test, a sample of the material is placed in a container filled with a solvent, which is sealed and then gently shaken. The sample is then left in the solution at room temperature for 24 hours. At regular intervals, the plastic is inspected for changes in measurement, texture, colour and dissolution. If the sample is very small, the test can also be conducted at the microscopic level. The sample is placed on a microscope slide onto which a solvent has been applied and then covered by a second slide. The drawback of the solubility test is that a number of plastics are dissolved by the same solutions. But if observations from non-destructive testing have previously been recorded, it may be possible to determine the plastic type based on the results of the solubility test.

The Hildebrand solubility parameter table (Appendix 8, page 201) is a good resource. If the difference between the solubility parameters for the polymer and solvent is less than two points, the polymer will dissolve in the given solution. The closer the parameters are to each other numerically, the more the polymer will swell in the solution.

3.2.2.1. Is it polyurethane ether or polyurethane ester?

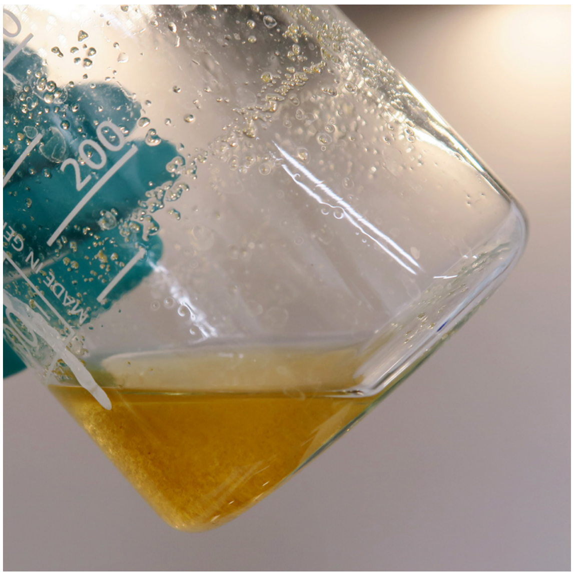
Many people don’t know that foam rubbers can be made from different kinds of polyurethane. One expanded plastic is hydrolysis-resistant (polyether polyurethane) while the other is susceptible to hydrolysis (polyester polyurethane). One tends to age as a result of oxidation and becomes brittle over time, while the other hydrolyses and becomes sticky. It is necessary to tell the difference between them for the purposes of preservation and conservation. This can be determined by the solubility test.

A 10% aqueous solution of sodium hydroxide (NaOH) or potassium hydroxide (KOH) is prepared. The requisite amount of chemical granules is added to deionised water (caution: exothermic reaction!) A sample of the material is then placed in the solution and heated for 15–20 minutes. Polyester-based polyurethane will dissolve, while polyether polyurethane will not.[117, 118] Be sure to wear protective gear (gloves, goggles, apron) as both NaOH and KOH are very caustic.



Boiling test pieces in a NaOH solution

Polyurethane ether remained unchanged even after 20 minutes of boiling



Polyurethane ester decomposed quite rapidly when heated in an aqueous solution of NaOH. Photographs by the author

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117 Castaneda, Adhesive Smackdown ...
118 van Oosten 2009: 81.

3.2.3. Test for identifying nitrocellulose

The diphenylamine or dip test can identify nitrocellulose plastic, film and varnish. The test requires diphenylamine ($(C_6H_5)_2NH$), sulphuric acid (H_2SO_4) and distilled water. Be sure to wear goggles, protective clothing and gloves while preparing the solution. Sulphuric acid is extremely corrosive and diphenylamine is very toxic. The solution should be made in a lab under a ventilation hood.

Diphenylamine reagent consists of 0.5% of the active ingredient in 90% sulphuric acid. If the concentrated sulphuric acid is 96% strength, it should be diluted with distilled water. Important: When diluting, always add acid to water, never water to concentrated acid. The reaction is exothermic. Once you have the desired strength of sulphuric acid solution, it should be carefully poured on to the required amount of diphenylamine granules. The result is a completely transparent bluish reagent, which is very corrosive and toxic and remains stable for about a year if properly sealed in a glass container and stored in the dark. The screw cap on the container must be acid-proof. Polyethylene and polypropylene are suitable materials for this.[119]

Diphenylamine reagent. Labelling should specify that it contains corrosive sulphuric acid! Photograph by the author

To carry out the test, take a sample from an inconspicuous place on the object using a scalpel and place it on a Petri dish. A sample can also be taken from the material by grating it against a roughened test tube. Then, using a pipette, place a drop of the diphenylamine solution onto the sample. Examine any colour change in the solution. Initially, the solution turns green. After about 20–30 seconds, a bluish tone can be seen, until finally the sample becomes lilac in colour. This confirms that it is nitrocellulose. The colour change can take more time if the nitrocellulose is very old (such as in the case of photo negatives). Additionally, a further control experiment should be carried out on a material confirmed to be nitrocellulose.

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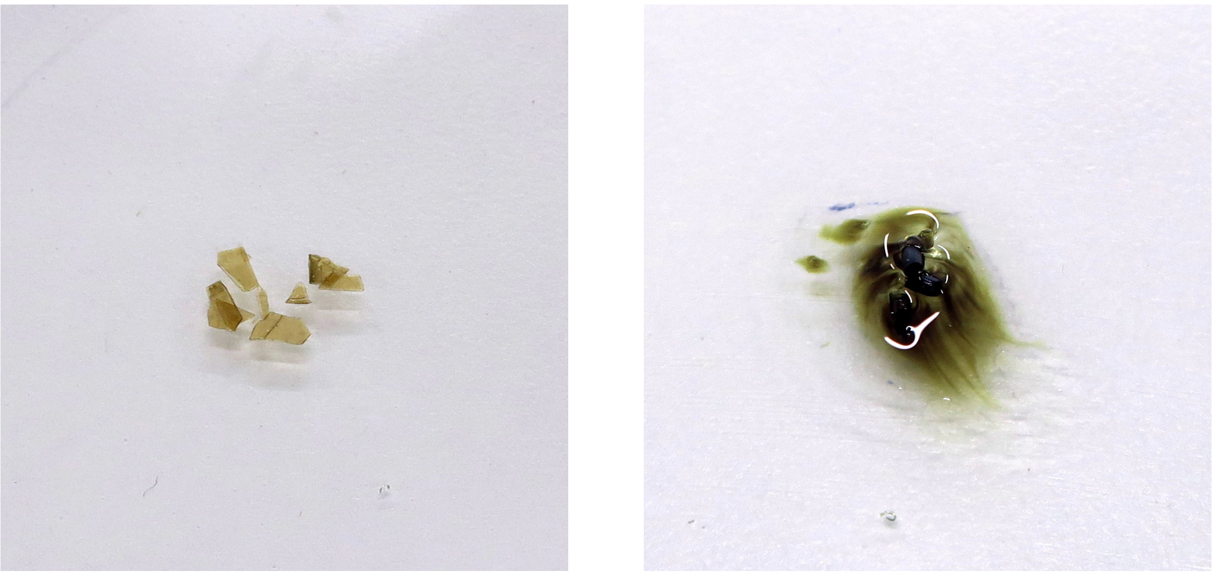
[119] Williams 1992.



Dip test. Initially green in colour, the reagent turns lilac after a short period of time when exposed to nitrocellulose.
Photographs by the author

3.3. Genuine or fake?

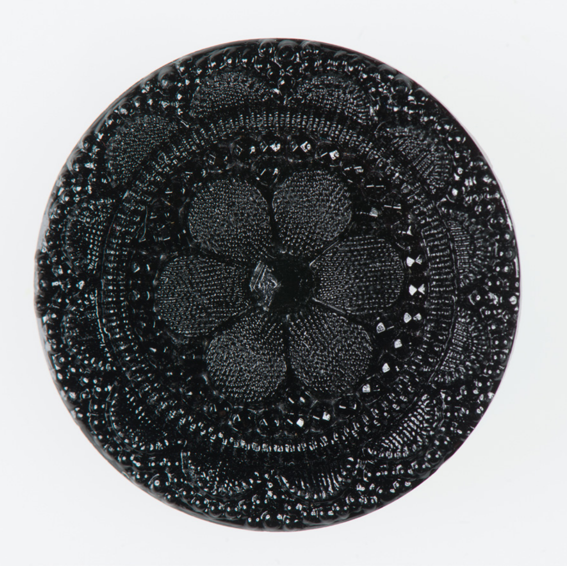
People generally don’t rack their brains inventing new materials for no particular reason. There is usually a specific purpose for research and the early plastics were developed due to a shortage of exclusively natural materials. Whether it was celluloid, which had to replace the ivory from elephant tusks, or phenol formaldehyde, which was developed as a substitute for shellac, these imitations are still capable of deceiving people today. The following sections discuss the most widely imitated natural materials and the plastics generally used to copy them.

3.3.1. Jet

In the late 19th century, jewellery made from black jet was widely worn during periods of mourning (especially in England). Ebonite was very well suited for imitating the expensive fossilised wood. It could be mass-produced at affordable prices, compared to jet, which had to be mined, cut and polished and which only the wealthy could afford.[120, 121]

In the 1920s, Bakelite was used for making jet imitations. It is superior to jet, which burns similarly to coal, as Bakelite tolerates high temperatures and resists most solvents. At the same time, Bakelite's mechanical properties were superior to those of jet.


Jet is fossilized prehistoric wood. Photograph by the author. The author's collection of samples


A button made of glass as an imitation of jet. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples


Necklace and chain made of polystyrene, designed to imitate jet and mother of pearl. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

Jet imitations were also made from black glass (French jet). Glass is cold and heavy. Synthetic thermoplastics like polystyrene and polypropylene, however, are very lightweight. One identification method is whether the material leaves a brownish stripe on a rough glass surface, albeit not an ideal test, because like genuine jet, Bakelite also does this.[122]

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120 Peters 2011.
121 Campbell, Plastics Imitating Gems.
122 Henney, Early Plastic Jewellery – Fakes and Forgeries.

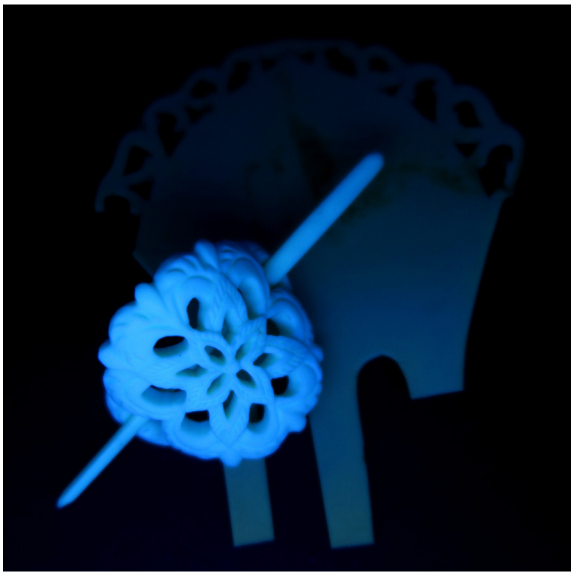
3.3.2. Ivory

The Hyatts came up with celluloid as a substitute for ivory and the result was very similar to the genuine item. Even Schreger lines, a characteristic of ivory, could be reproduced. Celluloid was made into the same types of items as ivory: boxes, jewellery, toiletries, etc. In addition to celluloid, galalith, melamine formaldehyde and polystyrene have also been used to imitate ivory.

Ivory hair clasp. Photograph: Anu Ansu and Berta Jänes. ERM A 902:29

An imitation ivory comb actually made of celluloid. Photograph: Anu Ansu and Berta Jänes. ERM A 645:10

Despite the fact that genuine ivory could be categorised along with gold and gemstones in terms of exclusivity, the production and sale of imitations has never been regulated. Sales of counterfeit ivory became particularly successful in the mid-1970s as it was then that restrictions on the export and import of ivory began. A fairly good method for distinguishing real ivory from imitation is to examine the item under ultraviolet (UV) light. Celluloid and galalith glow a vivid bluish-white, while real ivory will remain white (unless it is covered by a patina – in which case it will appear dull yellow-brown). If the colour under UV light is bright yellow, it may be artificially aged ivory which has been soaked in manure, urine or animal fat.[123]



Genuine ivory is radiant when exposed to UV light, in contrast to the celluloid imitation behind it. Photograph by the author

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[123] Chervenka, Ivory: Genuine, Fake, and Confusing.

3.3.3. Tortoiseshell

Tortoiseshell is obtained from the shells of the hawksbill sea turtle (*Erethmochelys imbricata*). They are an endangered species, up to 1 m in length and live in Atlantic and Pacific waters. The material obtained from the shells is prized for its workability and colour. Typical colour variations are dark brown and orange spots occurring irregularly on a light-yellow translucent background. As this is a thermoplastic (keratin), it can be melted and formed.

Genuine tortoise shell. Photograph: Anu Ansu and Berta Jänes. ERM D 39:47

Horn was the first material used to imitate tortoiseshell. It was difficult and time-consuming to attain a satisfactory result. Horn had to be boiled for a long time to remove its original colour and to make it softer. Then the horn was bleached with nitric acid to turn it a translucent pale yellow similar to amber. Finally, a dark imitation pattern was painted on the material. These tortoiseshell imitations made from horn bore a fairly accurate likeness to the genuine material. Only upon closer inspection could it be seen that the rippled pattern merely covered the surface.[124]

Tortoiseshell imitation made of horn. Photographs: Anu Ansu and Berta Jänes. ERM D 38:166, ERM D 38:167

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[124] Henney, Early Plastic Jewellery – Fakes and Forgeries.

Tortoiseshell imitations could also be made of galalith. Similarly to horn, the production process was time-consuming. It could be made much more rapidly and easily from celluloid. In the late 1920s, cellulose acetate imitations of tortoiseshell also appeared and are still used today, for example in eyewear frames.

Imitation tortoiseshell hair pin made of celluloid.
Photograph: Anu Ansu and Berta Jänes. ERM A 639:86

Imitation tortoiseshell eyeglass frames made of cellulose acetate. Photograph by the author

Items made of natural material were usually worked by hand, due to which tool trace marks can often be seen on their surface and the shape of the item itself may to some extent be uneven and asymmetrical. On the other hand, items made from nitrocellulose are symmetrical and totally smooth. And a ridge can be seen where the sides of the mould joined together. Smelling the item can also be of use: nitrocellulose gives off a camphor smell (a little like pine resin), while the natural material is odourless. Cellulose acetate has a vinegary smell.

Decorative stones or marquetry items made of artificial material have small holes bored into them beforehand for mounting. In tortoiseshell manufacture, these were simply pressed into the softened material. Artificial material is generally more flexible and lighter than genuine tortoiseshell.

3.3.4. Mother-of-pearl and pearls

Pearl and mother-of-pearl have been prized since antiquity due to their iridescence and complicated accessibility. It is not surprising that plastic imitations of these have also been attempted. Artificial pearls became particularly popular in the 1920s, when fashion dictated that strings of pearls should be many metres long.

Galalith yielded a very decent mother-of-pearl imitation. However, a significantly more popular imitation material was nitrocellulose, and a little later (from the 1930s), cellulose acetate. Items in great demand made from cellulose acetate included the handles of eating utensils, as well as hairbrushes, jewellery, shaving accessories, cameo boxes and much more. In more recent times, artificial pearls have been made of materials such as polystyrene, ABS copolymer and acrylic plastics.


Necklace of genuine pearls. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples


Imitation pearl earrings. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

Buttons made from genuine mother-of-pearl can easily be identified – on their reverse side is the dark and uneven exterior of the seashell. Weight is also an important indicator, as genuine pearls are heavier than imitations. Another clue is the shape of the pearls – genuine ones are never completely regular-shaped. Again, a good sense of smell can come in handy, as natural materials do not give off an odour.


Buttons made from seashells. The backs of the buttons can also be seen; these are of use in identifying the material. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

3.3.5. Coral

The hard calcium carbonate ($CaCO_3$) skeleton of red coral (*Corallium rubrum*) is a prized material and can be turned into attractive orange, red and pink jewellery and figurines. Red coral inhabits the dark, deeper reaches of the Mediterranean Sea.

The first imitation material was celluloid, and thanks to its excellent dyeability, the result was impressively close to natural coral. Once galalith emerged, imitations from this were also produced, and in the 1930s, from light-coloured phenol resin. Later on, imitations were made of melamine formaldehyde and polystyrene.

Imitation coral polystyrene necklace. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

Genuine coral feels colder and heavier than plastic. If the object is a darker red colour, it is worth looking inside for white stripes or patches – imitations lack these. A mould seam may be seen on close inspection of thermoplastics. And due to dye-casting, imitations made of thermoplastics tend to be symmetrical and identical to each other, whereas coral items are more variable. At the same time, “coral jewellery” was also produced from hand-cut and polished galalith and phenol.[125]

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[125] Collectors Weekly, Antique and Vintage Coral Jewellery.

3.3.6. Amber

This fossilised conifer resin has captivated humans for millennia due to its honey-coloured translucence and the insects and plant leaves preserved in it. Amber is common in the Baltic states, thanks to this prehistoric tree resin being washed ashore by the Baltic Sea.

Of the early plastics, the versatile celluloid was used to imitate amber, but phenol formaldehyde saw even greater application, due to its natural tone and transparency which already resembled amber. It was used to fashion transparent, slightly opaque, golden and also rare red amber imitations. Insects or flowers could be dipped into liquid resin very easily. Phenol formaldehyde imitations gained popularity in the 1930s. Later on, imitations have been made from epoxy resins and polystyrene.

Amber beads. Photograph by the author. ERM A 3717

Imitation amber pearls made of glass and polystyrene. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

Celluloid can again be recognised by its smell, if it is rubbed with a soft wool cloth. Another thing that should be noted when rubbing the material are its electrostatic properties – the surface of amber becomes electrostatically charged, while phenol resin does not. Another option is to see if the material will float in salt water. Genuine amber will not sink in salt water (about 2.5 teaspoons of salt per glass) and this is why it washes ashore on Baltic coasts. The heat test is used as a destructive identification method. A small sample of the material is taken and heated above a flame. Real amber will give off white smoke and a pleasant odour of burning pine wood. Phenol resin will char and give off a pungent phenol smell.[126]

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[126] Dragonfly Amber, How to Identify Real Amber from Imitations.

4.

AGEING AND DEGRADATION OF PLASTICS

It is often thought that plastics last forever and that conservation can be given short shrift. But a closer look at these “ageless” materials shows that in reality, they are actually susceptible to most environmental factors and degrade much faster than other materials.

A plastic item that appears to be in good condition may in fact be severely damaged. In the photo, the rubber figure has been degraded by oxidation. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

Plastic degradation factors can be divided into four groups: mechanical, physical, chemical and biological. Mechanical factors relate to the use of the item and improper storage/maintenance. Scratches, impacts, abrasion, distension – these can all harm the mechanical properties of plastics. As a result of physical damage factors determined by storage and usage conditions, the material’s appearance and mechanical properties can change. Chemical factors that contribute to ageing are oxygen, ozone, water, other chemicals, light and temperature. Biological factors are primarily microorganisms, insects and rodent activity.[127]

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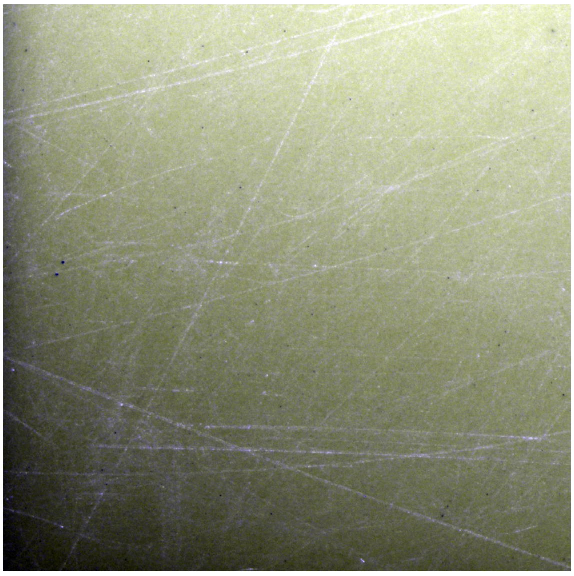
[127] Konsa 2007: 44–47.

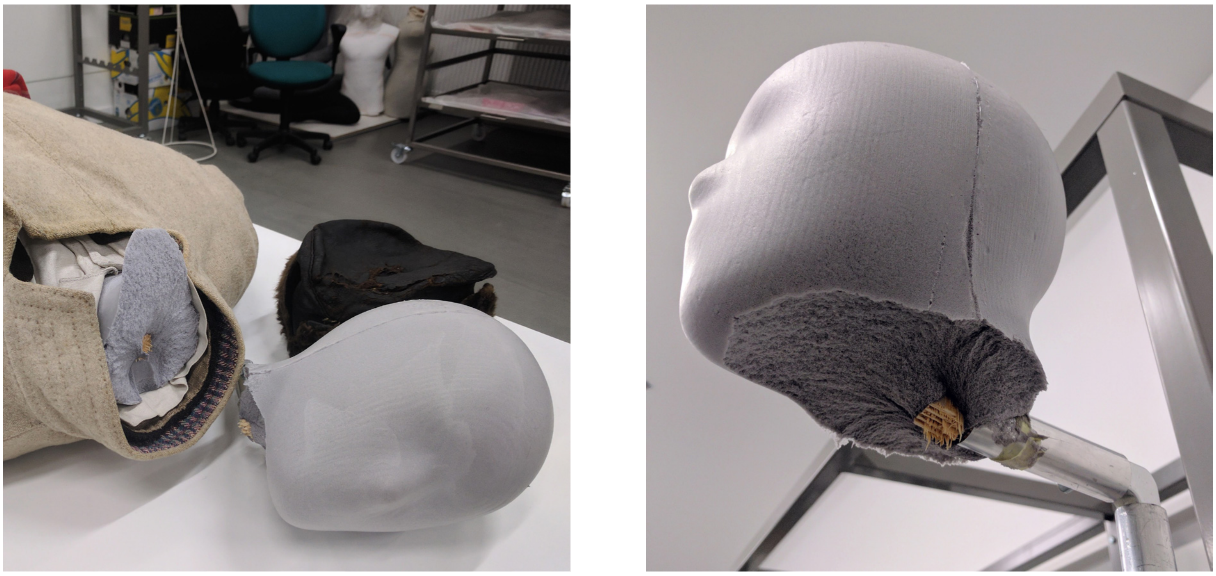
4.1. Mechanical damage

Whenever plastic is bent, stretched, compressed, dropped or abraded, the material can become deformed. For the most part, the initial surface damage is not noticeable. But a closer look at the surface reveals scratches that can harbour moisture, dirt and chemicals. Harmful agents penetrate into the marred surface. Consequently, the surface damage leads to internal degradation. Plastic items should be cleaned very carefully to avoid surface damage.



Ordinary dusting may create scratches on the surface of an object. They are visible under a microscope (polyethylene). Photograph by the author

If physical damage involves more significant bending, stretching, folding or mechanical stress, the result can be a visible deformity. One thing to remember about the ageing of plastic items is that one instance of damage can become complex, i.e. mechanical damage is followed by physical or chemical change and the latter is followed by more extensive mechanical damage.



Headless horseman – polyurethane foam that has been subjected to mechanical stress. Photographs by the author

Mechanical damage can also occur practically spontaneously, caused by the item's own weight, a phenomenon primarily affecting soft plastics – expanded plastics, PVC-P and rubbers. Quite often, we see that supporting areas of a soft object have become lopsided. Similar damage can be caused by items coming into contact with each other in storage. To prevent this type of deformation, soft plastic objects should be placed in a container on a padded supporting surface without other museum pieces resting on it.

Foam or hollow soft items may become deformed when they come into contact with other items and hard surfaces. Photograph: Anu Ansu and Berta Jänes

Soiling of an item can also be considered mechanical damage. This includes everyday dirt (dust, fingerprints, grime, mud, etc.), traces of pens/markers/paint including ones transferred from other items (e.g. being rubbed against each other). But if a permanent marker was used on the item and the pigment has migrated into the plastic, then the damage is already chemical in nature. This type of damage is discussed further in the section entitled "Labelling museum collection items" (page 133).

A heavily soiled polypropylene potty. Photograph by the author

4.2. Physical and chemical damage

An initial glance at a plastic item might suggest it is in good condition, like new, and undamaged in any way. The item may still be in its original packaging and completely unused. But if we take it out of the package, we may be in for an unpleasant surprise – a sticky, smelly, lopsided item that might even break when it is picked up. Many plastics react with moisture, oxygen, acids, bases and other chemical compounds. Even materials in the vicinity of plastic, such as metal, wood, leather, some surface treatments and other polymers, can have a detrimental effect.

A never-used doll still in its original packaging gradually experienced chemical aging. The plasticised PVC head has become sticky due to the plasticisers migrating to the surface. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

Physical damage includes deformations caused by moisture, temperature and light. It must be noted that the consequence of the damage does not involve a change in molecular composition; otherwise, the damage would be chemical. The four main types of chemical degradation are scission (breaking of polymer chains), cross-linking of polymer chains, the formation of light-absorbing compounds and formation of polar groups.[128]

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[128] Konsa 2007: 44.

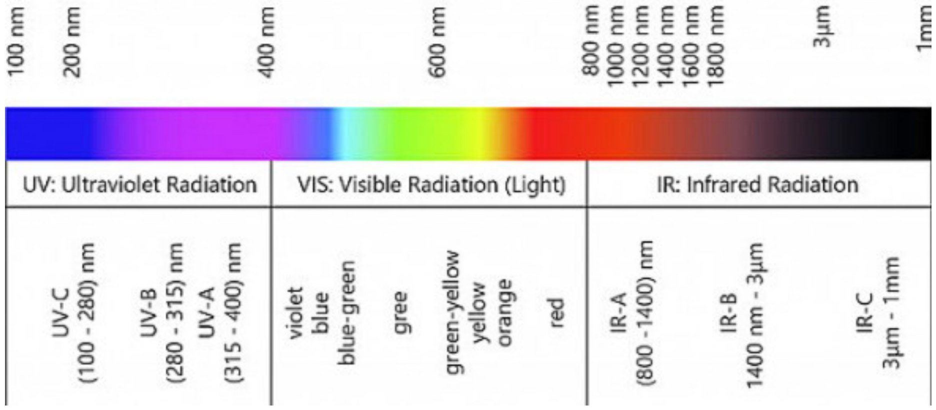
4.2.1. UV light and photochemical degradation

We need light to see objects. The Sun is of course the most essential light source for humans. Besides visible light (wavelengths from 400 to 800 nm), the sun gives off UV radiation, which activates a number of photochemical processes. Even though solar radiation is essential for life, it also causes damage. Sunburns, wrinkles, freckles, melanoma – thank you, Sun! And plastics are not happy either. They also suffer a number of effects due to UV radiation. In general, UV light breaks the chemical bonds in the polymers and damages pigments.

Most plastics exposed to UV light reflect it back. But if there are residual products from additives or damaged compounds within a polymer mixture, these can make them start absorbing harmful radiation. Free radicals gladly absorb radiation. The energy from radiation lets the free radicals bind themselves with oxygen and hydrogen, and thus generate new and incompatible molecular products.

The main agents in photochemical ageing are photons, the quantum units of electromagnetic radiation. Their job is to mediate interactions of electromagnetic radiation. The kind of energy the photons transmit, depends on the wavelength. For any photochemical process to take place, a certain frequency of radiation must be absorbed by certain molecules. This makes some polymers much more durable to UV light than others.[129]

The shorter the wavelengths, the higher the photon energy. In the infrared band (700–1,000,000 nm) photons do not carry enough energy to cause photochemical changes in materials. UV light with its high energy is the most aggressive. The wavelengths of UV light that reach the Earth from the Sun are no shorter than 290 nm. So under normal conditions, the main concern when it comes to preserving items is UV light with wavelengths in the range of 290 to 400 nm. It is worth knowing that UV rays with a wavelength of 315 nm and less are capable of penetrating ordinary window panes (UVA radiation).[130]



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[129] Feller 1994: 64.
[130] Feller 1994: 79.

When photons are absorbed by molecules, the transferred energy causes excitation of the molecules' electrons. There are five possibilities as to what happens next:

1. the excited molecule gives off the absorbed energy as heat;
2. the excited molecule gives off the absorbed energy as fluorescent radiation;
3. a change occurs in the chemical composition of the molecule;
4. the chemical bonds in the molecule break (photolysis);
5. the absorbed energy is transferred to another atom or molecule.

The first two results are photophysical processes and the last three are photochemical. The decomposition of molecular chains is not the main result of photodegradation. In actuality, the absorbed energy is transferred to nearby molecules. Molecules that otherwise don't accept photons at given wavelengths may thus become excited.[131]


It is clear which parts of the sewing machine cover (polystyrene) have had the most exposure to direct sunlight. Photograph: Anu Ansu and Berta Jänes

How can we be sure that a plastic object has been photochemically degraded? The most conspicuous guideline is the colour of the object, which has become yellowish in the areas exposed to light. Molecules excited by energy from photons have caused a reaction or have themselves reacted with other molecules, the result being a change in the molecular structure. The material or pigments now absorb and reflect light differently, due to which the object undergoes a change in colour. Some polymers absorb more light than others, for example polyurethane, polystyrene, polypropylene and polyethylene. Often a bluish pigment is added to plastic in the manufacturing process to keep the white looking "white" longer.

It should be remembered that photochemical degradation is irreversible. When some of the molecular chains have been broken, they cannot be "glued" back together into their original state. Fibres which have become fragile can be consolidated, by creating something like an exoskeleton around them, but we cannot reconnect the molecules. Fortunately, damage from light tends to be confined to the surface.

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[131] Feller 1994: 51.

4.2.2. Moisture damage

Moisture damage can be caused by too high (> 60%) or too low (< 30%) relative humidity (RH)[132] and sudden changes in humidity, or direct exposure to water. The extent to which RH or water affect an object depends on the polymer, additives, surface qualities and the conditions of the object. Polyamides are the most water-absorbent plastic, containing 3% water at room temperature. Under identical conditions, cellulose acetate contains 0.8% polymethyl methacrylate and polystyrene 0.1%.[133]

The effect of moisture must be taken into account when cooling and freezing, especially if the item is placed in a closable, airtight plastic bag. Condensation forms in a plastic bag if moved to a cooler environment. Along with absorbing excess moisture, contraction and direct contact with water, the beginnings of damage to the material are inevitable. Freezing of water is another problem. If the item has been accidentally scratched and condensation forms on it, freezing water entering through the cracks may damage the item.

The plastics most sensitive to moisture are cellulose esters, polyamides, semi-synthetic resin-based plastics and polyurethane ester foams. Plastics containing moisture-absorbing fillers (such as phenol formaldehyde, urea formaldehyde, or melamine formaldehyde) exhibit greater damage.

The handle of a knife made of melamine formaldehyde has been damaged by repeated exposure to water. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

Moisture accelerates ageing of materials. There are three main ways in which water is involved in degradation of polymers:[134]

- Hydrolysis of ester or amide bonds;
- formation of hydroxyl radicals or other chemical compounds;
- facilitation of the formation of ions (corrosion).

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[132] Relative humidity, abbreviated hereinafter RH.
[133] Shashoua 2008: 158–159.
[134] Feller 1994: 115.

4.2.3. Hydrolysis

Hydrolysis may take place if the object is in a moist acidic or alkaline environment. The item itself can cause the environment to become acidic, by giving off acidic substances or being next to an acidic material (e.g. a cardboard box that has become acidic). This mainly poses a risk to polymers that have groups of esters in their molecular chain – nitrocellulose, cellulose acetate, polyesters and polyester-type polyurethanes. Acidic compounds form in the course of ester group hydrolysis. The resulting degradation is the weakening of the material's structure due to broken molecular bonds.[135]

Hydrolysis of cellulose acetate results in the formation of acetic acid. Nitrocellulose gives off nitrogen compounds which form nitric acid when reacting with moisture in the air. Polyurethane ester foam becomes yellowish, fragile, sticky and cracked. Vulcanised natural rubber gives off hydrogen sulphide and other gases, and forms sulphuric acid on the surface.[136]

The nitrocellulose frames have become fragile in the course of hydrolysis. The silk paper used for preservation became acidic and very brittle over just a few years due to the nitric acid emitted. Photograph: Anu Ansu and Berta Jänes. ERM A 816:6

An aging rubber object gives off plentiful sulphur-containing compounds, as attested to the colour change in the indicator strip. ERM A 826:340. Photograph by the author

4.2.3. Thermal degradation

The higher the temperature, the faster materials degrade. Molecules are more mobile at higher temperatures and the bonds between them break more easily. Additives and gaseous compounds trapped by the lattices of the otherwise dense polymer chains start moving within the material. Various molecules also attack the heated material more easily than in cool conditions. "Newcomers" and "locals" can start forming new compounds.

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135 Shashoua 2008: 175.
136 Williams 2002.

The process where molecular bonds start breaking is called thermolysis. The higher the temperature rises, the more thermal energy molecules absorb. This energy makes the molecules vibrate. At a certain point, the vibration becomes so intense that the molecular bonds give way.[137] It is just like people dancing in a circle with wild abandon at some village festival – the faster the momentum and the more chaotically they spin, the harder it is to hold on to one another.

Temperature affects all plastics, but primarily ones with a low melting point, so thermoplastics are especially vulnerable. The first sign that an item has been exposed to high temperatures is a local colour change to yellowish brown. If the damage is more severe, the affected spot may appear melted or charred. Heat damage is a serious form of irreversible degradation. An object that comes into contact with excessive temperatures may become very brittle (such as a polypropylene bowl in a sauna) and retain its original shape, or it might become considerably deformed (e.g. a polystyrene container after a dishwasher cycle).

Leave a reel of film with the lamp on and the film will sustain local thermal damage. In this case, the material was cellulose acetate. Had it been a reel of nitrocellulose film, it would have caught fire. Photograph by the author

The first time it was washed in a laboratory dishwasher, a polystyrene measuring cup was deformed with stress fractures that clouded the otherwise transparent plastic. The wash cycle was at 90 °C while polystyrene melts at 100 °C. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

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[137] Feller 1994: 143.

Thermal damage may also appear when the storage temperature is too low. In this case, it is related to thermal expansion of materials. Every material shrinks when it is cooled according to its own parameters. If a plastic item is cooled properly and carefully, no problems should be expected. Plastic shrinks in the cold and returns to its original form at room temperature. Not so if an item contains more than one interconnected type of plastic or in conjunction with some other material. The joints can be stressed, and at worst, the item will experience mechanical damage.

4.2.4. Oxygen and oxidation

Any item should be kept away from heat, moisture and chemicals. Oxygen, however, is the substance that harms plastic the most. Since 21% of our atmosphere is oxygen, contact with plastic is unavoidable. The first damage occurs already in the manufacturing process, when plastic is in a molten state and oxygen has easy access to the polymer chains and other ingredients. The process whereby molecular chains bind oxygen is called oxidation.

The rate of oxidation is influenced by temperature, light, moisture and metal ions (Fe, Co, Mn, and Cu). The process starts with free radicals reacting with oxygen molecules. The peroxy radicals bind with any hydrogen in the vicinity, forming aggressive hydroperoxides.[138] These reactions occur more extensively in the case of polymers whose chain includes oxygen atoms, such as cellulose esters. Synthetic and natural rubbers are particularly vulnerable.

As a result of the oxidation reaction, the molecular chains break or the side chains bind with the main chain. The molecular mass of a polymer can thereby increase by picking up oxygen atoms, or decrease due to chain scission.[139] The plastic becomes brittle and rigid. Tensile strength and flexibility decrease and the colour turns yellowish-brown. For this reason, plastic can turn yellow even if it has never been exposed to UV radiation.[140]

Antioxidants can slow oxidation – these are substances which have mobile hydrogen atoms or can easily form a stable radical. Primary antioxidants react with peroxide and form relatively inert radicals. Secondary antioxidants remove radicals that activate the process. The most effective defence comes from photo-antioxidants, which prevent both oxygen and light from damaging the polymer chains. To a certain extent, fillers (such as carbon black) or special coatings can also serve as oxidation stabilisers.[141]

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[138] Loog, Timotheus, Järv 2012: 216–220.
[139] Horie 2010 [1987]: 40–41.
[140] Shashoua 2008: 171–175.
[141] Shashoua 2008: 71–72.

The foam rubber toy in the picture has experienced major oxidation, which turned it brittle and subject to crumbling at the slightest touch. The original colour of the fresh foam rubber can be seen in the image on the right. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

4.2.5. Plasticiser migration

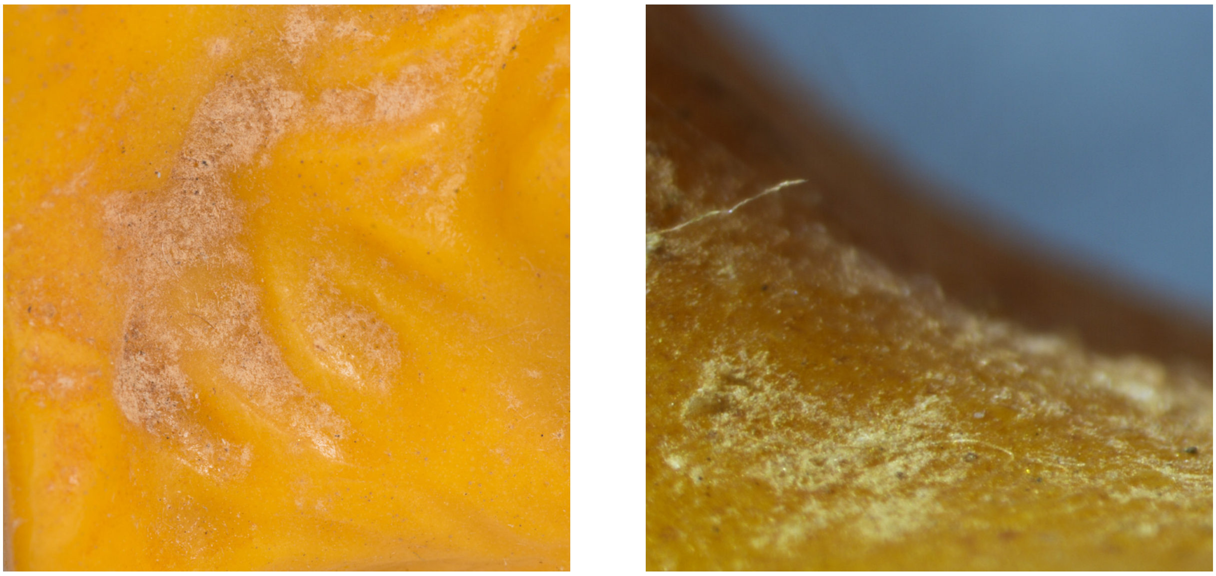
Energy from photons, high temperature, moisture, oxygen and other chemical compounds promote changes in the chemical composition of plastics. If intermolecular bonds are broken, they can react with other molecules within the plastic item or move to "happier hunting grounds" – migrating to the surface. Depending on the compounds, "migrants" either spread into the surrounding air or remain stationary and wait for suitable "partners". The main "voyagers" are plasticisers, antioxidants, stabilisers, and lubricants added to the plastic mix during manufacturing.

The plasticised PVC covers have become sticky and become stuck to the tissue paper used as a divider. Photograph by the author

Camphor, used as a plasticiser for nitrocellulose, migrates to the surface as a result of crystallisation and vaporises over time at room temperature. Liquified plasticisers remain sticky on the surface of the item and become more susceptible to dirt, moisture and harmful compounds. Phthalates are added to cellulose acetate and polyvinyl chloride as plasticisers. Depending on the quantity of plasticiser added and the preservation conditions, a sufficient quantity can eventually migrate to the surface of the material and cause it to weep.

Besides plasticisers, lubricants may also migrate to the surface. For example, the stearic acid used to facilitate PVC-P production can gradually form a greyish-white coating on the surface. It can easily be mistaken for mould. Over time, antioxidants may also migrate, as observed in vulcanised rubber that has been wrapped in light-coloured cloth or paper. This is indicated by yellow spots eventually forming on the wrapping.

Migration doesn’t always take place from the inside out. An important consideration in the storage of plastics is the surrounding environment and the kinds of materials and substances they may come into contact with. For example, polyethylene and polypropylene absorb oils and volatile organic compounds. For that reason, food storage containers appear to become “greasy” after prolonged use. Plasticised polymers readily absorb adhesives and pigments through contact.



A crystallised layer of lubricant has formed on the surface of this plasticised PVC item. It can easily be removed by wiping. Photographs by the author

The masking tape strip on the leg of the plasticised PVC doll and the inscription made on it has caused irreversible damage as the adhesive in the tape has reacted with the plasticisers. The marker inscription has migrated through the tape into the plastic. It took only six months for the damage to be done. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

4.2.6. Damage caused by polymer dissolution

When undertaking conservation work – be it cleaning, consolidation or gluing – it is extremely important to understand the solubility of polymers. This is precisely the stage where there is a risk of damaging the material by using the wrong solvent. Never clean the surface of nitrocellulose items with acetone, as celluloid dissolves very easily in this solvent and surface damage is inevitable. Actually, acetone should also be kept away from other plastics – polystyrene, polycarbonate and polymethyl methacrylate are all very vulnerable to it. To find out which solvents can dissolve which polymers, consult Hildebrand solubility parameters for organic liquids and polymers (Appendix 8, page 201).

Acetone dripped on the surface of the CD-case (polystyrene) has caused irreversible damage. Photograph by the author

Additional information on the solubility of polymers is provided in Appendix 7, page 200. As molecular mass increases, solubility decreases. The density of the polymer chains at the molecular level is also important. Amorphous polymers dissolve better than crystalline polymers. Crystalline polymers dissolve when heated to their melting point. For instance, polyethylene does not dissolve in any solvent at room temperature, but does so in several solvents at 100 °C.[142]

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[142] Rosen 1993: 84.

4.3. Biological degradation

Changes in material properties caused as a result of living organisms are termed biological damage. Microorganisms such as moulds and bacteria are classified as biological agents. Of course, insects and rodents also fit this description. If their teeth fit around the object, these pests can cause mechanical damage to any plastic items. Dogs, too, like to chew on plastic. A subsection provides information on species of mould and their effect on plastics.

Biological agents generally attack natural and semi-synthetic plastics, such as casein formaldehyde (based on milk protein) or nitrocellulose (derived from cellulose). In synthetic plastics, additives attract microorganisms. In regard to additives, plasticisers have been studied the most – especially the ones added to PVC. Plasticisers are esters that are quite vulnerable to microfungi. The most common mould species that attacks PVC-P is *Streptomyces rubrireticuli*, which leaves a pink stain on the surface of the plastic. As well as pink staining, surface mould appears on PVC and nylon, caused by *Penicillium janthinellum.*[143]

Under cover of darkness, a pet rabbit decided to nibble on the nose of the doll. Photograph by the author

Buttons made of casein formaldehyde have mildewed in a warm and humid environment. Photograph: Anu Ansu and Berta Jänes. ERM A 984:86

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[143] Allsopp, Gaylarde, Seal 2004: 65–77.

Visual damage is not the only consequence. The mould covers the item's surface, thereby changing the plastic's surface properties, a departure from the way the material would ordinarily react with the environmental conditions. As mentioned, a number of microfungi feed on additives. Starting its life cycle on the surface, they "suck up" plasticisers and additives and change the plastic's composition. As a result, microfungi render the surface acidic. Binding moisture, microorganisms create a favourable environment for hydrolysis of the plastic, as a result of which the polymer chains break. On top of it all, mould also damages colour pigments.[144]

Microfungi need a moist, acidic environment for growth. Just a trace percentage of moisture in the material is sufficient for mould and bacteria to start proliferating. Consequently, hydrophilic polyamides and casein formaldehyde are susceptible to mould, while polyethylene and PTFE (Teflon), being hydrophobic, are impacted less. However, mould can spread over the surface of an otherwise hydrophobic plastic if the surface is rough or scratched. In such a case, dust or dirt adheres to the surface, binds moisture and thereby creates a favourable environment for mould growth.[145]

Plastics that have aged or been subjected to mechanical load are less resistant to biological agents. HDPE attests to this: its polymer chain is basically an unbranched "spine", which makes it particularly resistant to mildew (only the ends of the chain can be attacked). But if a piece of polyethylene is first chemically degraded and then introduced into a bioactive environment, it will visibly aggravate the damage. Polymers with less branching and crystalline polymers are more resistant to microorganisms, since they are also more resistant to mechanical, physical and chemical damage.[146] Biodegradable plastics are produced precisely to be less resistant to oxidation and break down quickly into smaller "bite-size" pieces. Starch can also be added to biodegradable polyethylene to make it hydrophilic.

A layer of mould has formed on nitrocellulose film stored in damp conditions, damaging the footage. Photographs: Anu Ansu and Berta Jänes

One Estonian National Museum permanent exhibition showcase demonstrated a dripping sink – a fixture of many Soviet-era memories, along with cleaning compounds. Over six months, microorganisms in this moist and warm incubator managed to colonise all of the materials – even the polyethylene bottles. Photograph by the author

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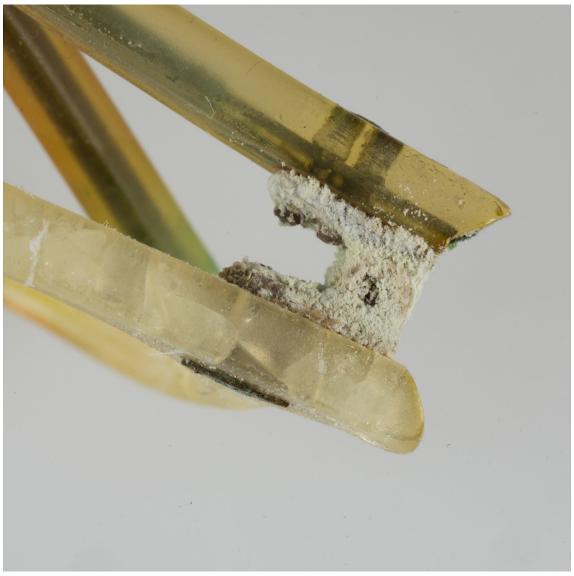
[144] Cappitelli, Sorlini 2008.
[145] Muthukumar, Veerappapillai 2015: 204–209.
[146] Allsopp, Gaylarde, Seal 2004: 70.

4.4. Five “malignant” plastics, their risk level and proper conservation

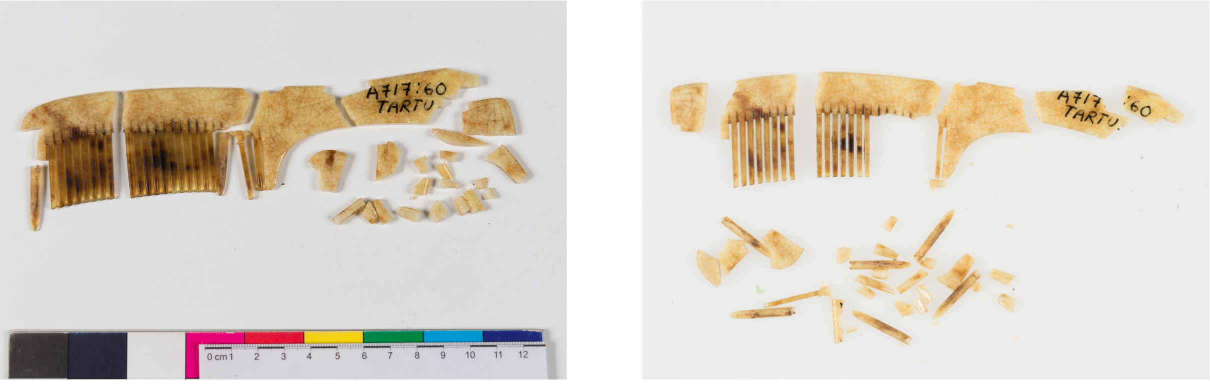
For the plastic conservation novice, the number of different plastics found in museum collections can seem mind-boggling. The five plastics below should definitely be memorised, as they’re on the list of malignant plastics for a good reason. Back in the 1990s, a number of museums noticed that certain plastics not only aged faster than others, but gave off harmful compounds that also degraded other materials (such as paper, metal and textiles). The compounds emitted during degradation can also be harmful to human health.

4.4.1. Nitrocellulose

Nitrocellulose ranks at the top as a malignant plastic, due to the fact that it gives off nitrogen oxides as it ages, which then react with water vapour to form nitric acid (HNO_3). The acidic compounds damage pigments in nearby items and corrode metal. If we were to place a degrading celluloid object into a sealed environment (a closed box, wrapped in paper, etc.), over time, the acid could cause the item to crumble.[147]



Nitric acid given off by nitrocellulose corrodes nearby metals. Photograph: Anu Ansu and Berta Jänes. ERM A 853:57



Over three years, a nitrocellulose comb has degraded visibly. Photographs: Arp Karm, Anu Ansu and Berta Jänes. ERM A 853:57

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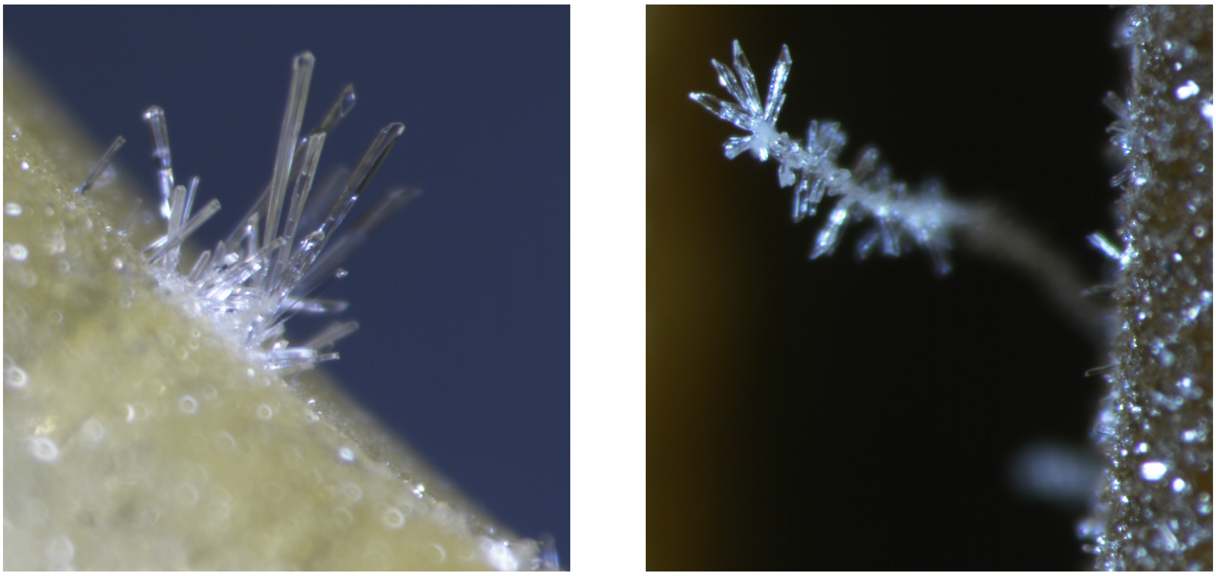
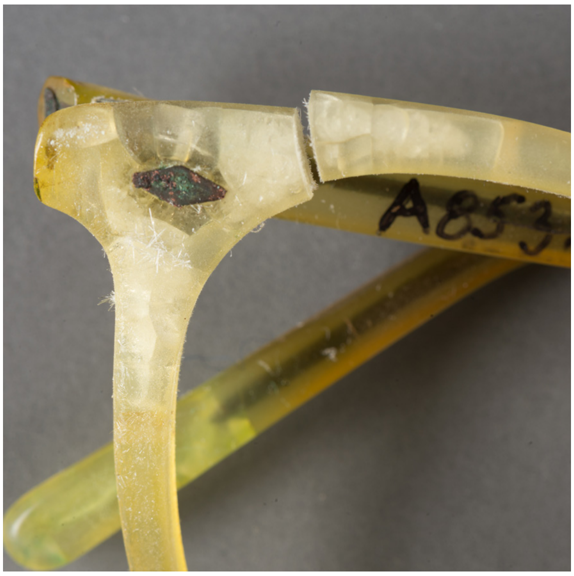
[147] Tsang 2010: 20.

The release of nitrogen compounds in an alkaline environment may lead to precipitation of sodium nitrate or potassium nitrate crystals. They start “growing” on the surface and in the vicinity of the object, posing a threat to adjacent items.

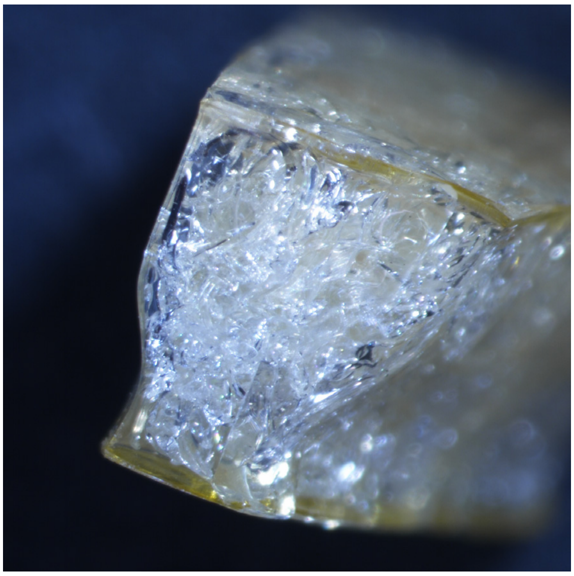
Non-nitrogen compounds are not the only kind released by nitrocellulose. The camphor used as a plasticiser also tends to migrate out of the celluloid. During degradation, nitrocellulose crystallises. The material shrinks and the camphor is forced to the surface. Structural cracks develop in the item. The cracks formed during degradation are a pathway for nitric acid to start penetrating the nitrocellulose.[148]



Nitrate salt crystals on the surface of nitrocellulose items. Stereomicroscope image, 45x magnification. Author’s microscope photographs



Nitrocellulose crystallised as a result of hydrolysis. Photograph: Anu Ansu and Berta Jänes. ERM A 853:57



Author’s microscope photograph

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[148] Shashoua 2008: 179.

Another key reason that nitrocellulose is considered “malignant” is its flammability. Guncotton (pyroxyline), which was originally used as an explosive, has basically the same chemical composition as nitrocellulose. The difference lies with the additives and the amount of nitrogen – celluloid plastics contain 10.5–11.5% nitrogen; while varnishes, sheets of film and rolls of film have a level ranging between 11.5–12.3%; and explosives, 12.4–13.5%. The nitrogen content of cinematic film is higher than that of photo negatives and sheets of film made of nitrocellulose.[149] It is worth noting that the self-ignition temperature of sheets and films is only 40–50 °C above room temperature. Nitrocellulose’s degradation process is exothermic. If there are many ageing film reels stored together, the temperature in the immediate proximity can rise to a point where they can burst into flame. Nitrocellulose burns with a flame 15 times hotter than wood, and the flame cannot be extinguished with water, as the combustion reaction itself feeds the fire with oxygen. The combustion also releases a large quantity of toxic and explosive gases, which ignite in the flame. This makes early films very dangerous and they require special storage conditions.[150]

Items made of nitrocellulose must be stored in well-ventilated rooms. Under no circumstances should artefacts be stored together with museum pieces made of metal, textiles and paper. Materials that bind acidic substances (such as activated charcoal and zeolites) should be placed in storage containers. There is no point in adding oxygen absorbers to the package, as nitrocellulose gives off a certain amount of oxygen naturally as it degrades. A drawback of using Ageless packets is that the formation of ferric oxide releases water, which raises the humidity inside the package and promotes hydrolysis. The storage room should have a sufficiently low and stable relative humidity (~40%) and low temperature (< 16°C).[151] Instructions for the preservation of items that have become acidic can be found in *Section 5.2.7.2. Packaging of museum items that give off acidic compounds.*

4.4.2. Cellulose acetate

The degradation of cellulose acetate is somewhat similar to that of nitrocellulose. Plasticiser migration causes the plastic to shrink, become sticky and fragile; film reels and negatives will start curling and become deformed. Due to the acetic acid given off as a result of hydrolysis, the process is termed “vinegar syndrome”. As much as 6 ml of acetic acid can be released from a metre-long length of acetate film in the course of advanced ageing. The rate of acid emission doubles if the pH has dropped to 4.6.[152] Besides acetic acid, cellulose acetate also gives off sulphuric acid. Acidic gases are particularly damaging to nearby metals, textiles and papers. As an eye, nose and upper respiratory irritant, they are also harmful to humans (just a few hours of exposure to ageing acetate films in a poorly ventilated room can cause a stinging sensation in the nose).[153]

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[149] Fenn, Williams, Caring for plastics and rubbers.
[150] Heckman 2010: 483–506.
[151] Williams 2002.
[152] Shashoua 2014: 13–15.
[153] Shashoua 2008: 179–184.

When an aluminium container in which photo negatives was opened, a strong vinegar scent was immediately detected. Within 24 hours, an acid-detection test (A-D Strip) turned green, showing that the negatives had become acidic in the sealed environment. Photographs by the author

Unlike nitrocellulose, the plasticiser given off by cellulose acetate (mainly diethyl phthalate, DEP) remains on the surface of the item, making it sticky. Thus, film can become stuck to itself. Items can also adhere to other museum items or packaging.[154] According to research, DEP may cause neurological harm and impact genital development in the foetal stage.[155] These studies were conducted in testing of food and cosmetics industry products to which many people are exposed daily.

Items made of cellulose acetate must be stored under similar conditions to nitrocellulose. It has been observed[156] that the migration of diethyl phthalate to the plastic surface does not depend on relative humidity level or fluctuations in relative humidity. Knowing that can come in handy when looking for the happy medium for storage conditions. Plasticiser migration does depend on the pH level of the plastic and its nearby items. A low pH will speed up the rate of plasticiser emission.

4.4.3. Plasticised polyvinyl chloride

The "malignancy" of items made of plasticised polyvinyl chloride is related to the release of plasticisers and additives from the polymer chain. The most common type of plasticisers are phthalates, which form weak bonds with the polymer. This makes it easy for them to break free of the molecular chain and migrate to the surface, forming a sticky layer that traps dirt, chemicals and moisture. In the 1950s, di(2-ethylhexyl)-phthalate (DEHP) began to be added as a plasticiser, but it was banned in the EU in 2006. At room temperature, DEHP vaporises very slowly from the surface of the item.

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[154] Mccormick, Schilling 2014: 10–12.
[155] Bornehag et al, Prenatal Phthalate Exposures and Anogenital Distance in Swedish Boys.
[156] Richardson et al 2014: 231–236.

Over time, so much of the oily plasticiser can accumulate on the surface that it can start dripping from the item. DEHP can trigger allergic reactions. Longer-term exposure may harm the immune system, increase the risk of liver cancer, reduce fertility, and contribute to obesity. DEHP imitates oestrogen, thus altering the body's hormone levels.[157, 158] Anyone who is frequently exposed to ageing PVC-P items should be aware of this. Latex or nitrile gloves must be worn when handling such items. Be sure to wash your hands if handling them without protective gear.

A PVC-P Barbie doll has become sticky due to plasticiser migration. Photographs: Anu Ansu and Berta Jänes. The author's collection of samples

A coating of a crystalline substance can form on the surface of PVC-P, caused by lubricants added to facilitate production, or crystallised phthalates formed during hydrolysis. The coating is called "bloom". The substance in surface bloom can damage items it is in contact with, causing staining or corrosion.[159]

In addition to plasticisers and lubricants, hydrogen chloride (HCl) — a colourless, water-soluble gas — is released from PVC-P, which forms hydrochloric acid when it comes into contact with moisture.[160]

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[157] Bornehag and others, Prenatal Phthalate Exposures and Anogenital Distance in Swedish Boys.
[158] European Commission 2008.
[159] Shashoua 2001: 41.
[160] Shashoua 2001: 18.

Items made of PVC-P must be stored separately from other items in the museum's collection. The room should be cool (< 16 °C) and fairly dry (RH ~40%). Plasticisers will readily migrate to a less dense environment (the air next to the surface) and they are especially prone to accumulating in absorbent materials. So if a PVC-P item is packed in crepe paper, the paper will absorb the plasticisers. This however encourages additional plasticiser migration, as there is now more available room on the surface of the item for the molecules seeking their freedom. Polyethylene film is also an absorbent material, so there is a risk of accelerating plasticiser migration by packaging a polyvinyl chloride item in e.g. a Ziploc bag.[161]

As to whether it is better to store PVC-P items in a well-ventilated room or sealed container, there are various points of view. General guidelines recommend providing good ventilation to prevent HCl from accelerating up ageing, but there is also evidence that HCl accumulating in a sealed package reaches saturation point and curtails migration. As a result, the recommendation is to store PVC-P items in a non-absorbent sealed package (e.g. made of glass). Activated charcoal and silica gel should definitely not be added to the sealed package, as these will absorb plasticiser in addition to volatile organic compounds and moisture.

4.4.4. Polyurethane foams

The main hazard associated with polyurethane foams is related to thermal degradation: if the plastic has been exposed to too high a temperature, the polymer's molecular structure breaks down into volatile compounds. Primarily, this takes place during production processes (both production of raw material and the manufacturing of items). The thermal degradation of some polyurethane materials can start at just 150 °C. Thermal degradation can be caused by welding, charring, heating, hot air blowers, hot wire-cutting, hot scissor-cutting, polishing and sawing. It also takes place when the material is ignited.[162]

All materials, both natural and synthetic, give off hazardous chemical compounds when burned. Therefore, it is important to know how easily a material ignites. Polyurethane foam is intrinsically easy to ignite, while polyurethane ether used for mattresses and upholstery ignites more easily than polyurethane ester. The following chemicals are released during combustion: carbon dioxide, carbon monoxide, nitrogen oxides, hydrogen cyanide, isocyanates, amines and hydrocarbons. Exposure to these gases may cause stinging of the eyes, nose, and lungs, dizziness, headaches and general malaise. Polymer mixtures are treated with flame retardants to slow ignition.[163]

Bear in mind that ageing polyurethane ester gradually releases irritating and harmful acidic gases even at room temperature. Thus it is wise to monitor foam items in collections and occasionally check acidity levels; the best course is to keep them separated from other items.

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[161] Shashoua 2001: 28.

[162] van Oosten 2009: 42–45.

[163] American Chemistry Council, Center for the Polyurethanes Industry 2014.

Degraded polyurethane ester foam can also be considered “malignant” due to its stickiness. As it becomes crumbly and sticky, the foam adheres to surfaces it touches, potentially resulting in staining and damage. For example, if a thin layer of foam has been used as an insulating layer for a coffee pot warmer, it should be removed. This type of foam has a service life of 30–40 years at best. Removing sticky and crumbly foam is an arduous task. The compounds released stain textiles, and if it comes into contact with woollens that cannot be wet-cleaned due to risk of pigment loss, removal of ageing polyurethane foam can be a real challenge.

Polyester-based polyurethane foam was used as a padding material in a Soviet-era aviation helmet. Over time, it has become crumbly and sticky due to hydrolysis. Photographs by the author

4.4.5. Vulcanised natural rubber

Vulcanised natural rubber is harmful to its surroundings due to the volatile organic compounds (VOCs) it releases. The large quantity of sulphur used in the vulcanisation process is released over time as gases (e.g. hydrogen sulphide, H_2S, and sulphur dioxide, SO_2). These compounds account for the specific rubber odour.

In the process of oxidation, natural rubber’s polymer chains undergo either cross-linking or, conversely, molecular chain scission. In the case of cross-linking, the material becomes solid and fragile, and foam rubbers start to crumble. Chain scission, on the other hand, results in softening of rubber. Shorter chains form ketones, aldehydes, acids and hydrogen peroxide. The formation of such compounds is more extensive in hollow rubber objects, as the gases collect inside them over time. The ever faster oxidation triggered in this manner transforms thermosetting natural rubber into, essentially, a thermoplastic, since an item made of it becomes sticky and appears melted. Yet it is not actually a change in the phase, but rather transformation of the characteristics of the material under the right conditions.

As a result of oxidation, the material properties of the natural vulcanised rubber have changed. Consequently, the rubber appears as though it has melted, and the material has become partially sticky at room temperature. Photograph by the author

As a result of oxidation, a rubber pump became brittle, much like unfired pottery. This could have been prevented by storing it in a low-oxygen environment. Photograph: Anu Ansu and Berta Jänes. ERM AM 100:1

Vulcanised rubber objects must be kept separate from other museum items (especially silver and copper), placed in a well-ventilated room or in a box containing acid-absorbing materials. By lowering the relative humidity, the rate of sulphurous acid (H_2SO_3) formation will decrease as well. Ageing rubber items must not be allowed to touch each other. If it is necessary to fold the item (such as raincoats etc.), sheets of an inert non-tacky material (e.g. polyester film) should be placed between the layers.

To slow down oxidation, actively ageing objects are placed into airtight oxygen-free packaging. This kind of preservation method lends itself to items that do not have to be examined or handled very often. The fact that an oxygen-poor environment slows degradation of natural rubber was demonstrated by a study conducted by the British Museum. The condition of rubber items placed in airtight packaging from 1991 to 1995 was investigated 15 years later, and the condition of correctly packaged items was the same as that prior to packaging.[164]

To aid in understanding damage to plastic items, consult the table on the most common forms of degradation and damage to plastics (Appendix 6, page 194).

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[164] Dyer and others 2011.

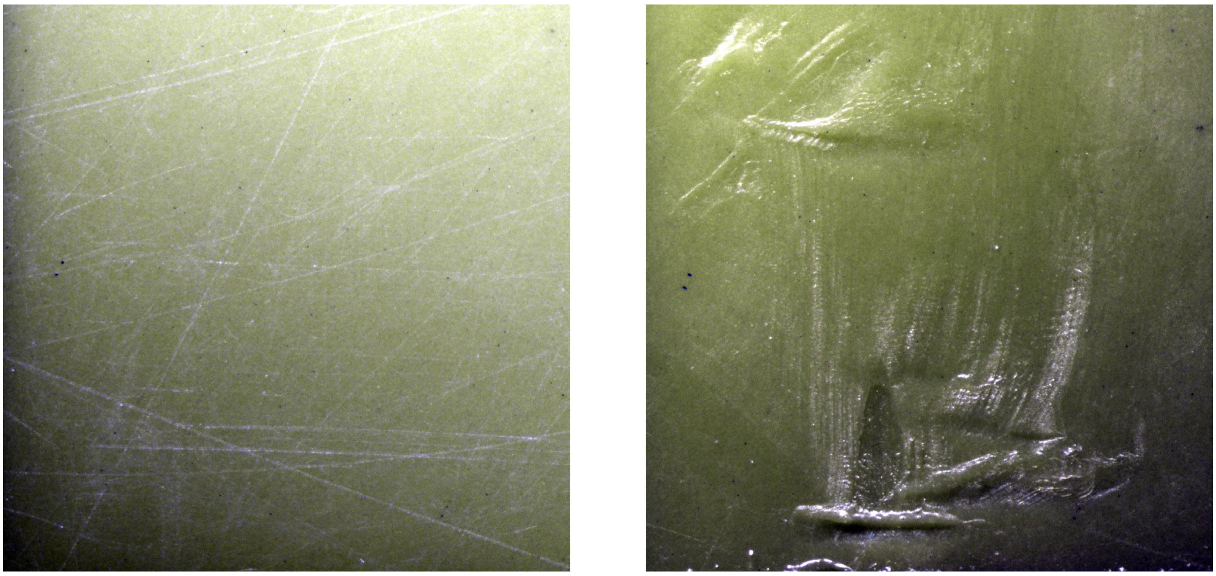
5.

PREVENTIVE CONSERVATION

Chemical and physical damage to plastics is inevitable. Plastics are organic materials that react with nearly everything that surrounds them. If only they all reacted the same way, it might be easier, but in fact some are water-sensitive, others are influenced by light, a third group is attacked by oxygen and the fourth have paired up with the agents of degradation themselves. The task confronting conservators is to find out which conditions speed up the ageing of plastics and what should be done to prevent damage to plastics.

The practical conservation of plastics is only a few decades old, which is not enough time for solid conclusions and definitive protocols to take shape. We still cannot be sure whether a repair made today will not cause damage after a few years. That is why preventive conservation has a very important role in preservation of plastic items.

Preservation of an item starts from the moment we pick it up. Any handling of an item poses a potential risk. For example, during the initial investigation, an item may be dropped or break during handling, the evaluator's fingernails or jewellery may scratch the item, fingerprints are left on the surface when touching it with bare hands, etc. Therefore, plastic items should be touched as little as possible. Age-degraded plastics may be very brittle. Handling requires a delicate touch and attentiveness. Forget any claims about the material being unbreakable.



Some plastics like polyethylene are sufficiently soft to be scratched by fingernails. Photographs taken under a microscope show the same location before and after. Photographs by the author

Wear gloves. Bare hands will leave oily fingerprints on the item that will attract dirt. It is best to use either latex or nitrile gloves. Cloth gloves may leave fibres sticking to the surface of the plastic item. Fabric gloves are also slippery, so be vigilant when picking up a smooth plastic item. If the use of gloves is not possible for some reason, hands should be carefully washed after handling the item. Substances hazardous to human health may migrate to the surface of several kinds of aged plastic. Rings and bracelets should be removed. When lifting an object, use both hands and never lift an object by its handles as they may have become brittle.

5.1. Evaluation of the condition of plastic items

Evaluation of the condition of an item requires experience and attentiveness. The person evaluating should know what kinds of damage could affect plastics and learn to recognise them in practice. At the same time, an ability to identify materials is also necessary. Greater attention should be given to malignant plastic objects, as they often age more quickly. When making an assessment, all types of damage (mechanical, physico-chemical and biological) must be taken into account. These should all be considered separately in the assessment, as each category consists of a number of types of damage, with different implications for the durability of the plastic.

A five-point evaluation scale is recommended. In the case of rapidly ageing materials, the common three-point scale (good, fair, poor) is too limited for plastics that can deteriorate literally overnight.

An evaluation of the condition of plastic items requires knowledge of the causes of specific damage. In this case, shoe soles made of elastic polyurethane have become brittle so they break when bent. The surface has also become sticky, showing advanced chemical degradation leading to mechanical damage. Photograph: Anu Ansu and Berta Jänes. The author's collection of samples

Condition scoring:

5. **Very good** – The item is new (or appears new) without any damage or very minor surface soiling that is easily removed by dry dusting.
4. **Good** – The item has minor surface damage (scratches, nicks), the surface is slightly soiled and there is minor photo-degradation (yellowing or bleaching). The condition of the item is stable and surface dirt can be removed. The item is intact.
3. **Fair** – The item has surface damage (scratches, nicks, dirt) and photo-degradation (yellowing or bleaching). There may be some cracks, splits, gaps or minor deformation (for example, collapse of the item’s supporting surface). The item may have early-stage chemical, physical or biological degradation.
2. **Poor** – The item has major mechanical degradation, photo-degradation is extensive. There are broken and deformed areas with some missing parts. Extensive chemical and physical ageing has taken place. To some degree, ageing can still be brought under control. Depending on the type of plastic, the item may be hazardous to other museum items, in which case it should be removed from them and stored under special conditions.

1. **Very poor** – The item is severely mechanically, chemically, physically and/or biologically degraded. Its shape is severely deformed and some parts are missing. Ageing is so far advanced that the aim of preservation should perhaps be reconsidered. Ageing is taking place very rapidly and it is either complicated or impossible to halt.

The seriousness and extent of the damage should be the basis for assigning the overall score. For example, a scratched doll made of polyethylene which is missing an arm and whose chemical condition is stable cannot be given a score of 2 (poor) simply due to its physical damage. Chemical stability is an important consideration, so even if the doll is missing parts and no longer looks as it originally did, preservation is not that big a problem. However, if we have a PVC-P doll with identical mechanical damage, it could indeed be assigned a 2 (poor) because of plasticiser migration. This doll's chemical condition is poor and affects its mechanical integrity. The doll is subject to special storage conditions and must be kept separate from other items. To resolve these types of situations, it is important to know the various kinds of damage that can occur in plastics and how they influence the preservation of the object (see Appendix 6, Most common types of damage to plastics, page 194).

The following are the correct steps for preparing an assessment of the condition of a plastic museum piece:

1. **Identification of the polymer** – to evaluate the condition of a plastic item, the material should first be identified. Different plastics age at different rates and to a different extent. The ability to identify "malignant plastics" is important.
2. **Integrity and physical condition of the item** – upon first inspection of the exterior, scratches, dents, broken areas and missing parts may be detected, and then more than likely mechanical damage and the lack of integrity. If these kinds of problems are already visible to the naked eye, the rate of damage is high.
3. **Physical and chemical damage** – does the item appear to be fragile, is damage from light visible, fragility of the item, stickiness or some other physico-chemical damage visible?
4. **Biological damage** – does the item have mould growth or chew marks?
5. **Scoring and decision**

If the score is between 5–4, there is no reason for concern. The item can be placed in stable storage conditions or be exhibited.
If the score is 3, it should get regular attention and the damage will need to be addressed quite promptly (whether as practical conservation or special preservation measures). In the case of some polymers that are more unstable, it is likely that special conditions must be used for their display and that the object may no longer be suitable as an exhibit at a permanent exhibition.
If the item's condition is 2–1, it is a severely aged item and preservation will be complicated. An item with a score of 1 may have completely lost its original appearance and function.

An inspection of actively ageing plastic items should be conducted every six months, and in some cases even more frequently. Yet moving and touching an ageing object in any way is harmful – items may collide with each other if a box is moved, dirt and debris shed by one item can scratch another, careless handling can result in a dropped and broken item. To make the appraisal safer for the objects, it is good to know where and in what state the museum pieces that will undergo inspection are. After appraisal, plastic items with a different degree of ageing and those made of similar materials should be divided into corresponding boxes, which minimises handling of items that do not need to be inspected at a given time.

To make it easier to score plastic items, see the worksheet in the appendices. The table can be used as a printout, but it would be preferable to access it on a tablet or other device so that any images of damage could be added on a rolling basis. It also makes it easier and more convenient to enter information into the table.

5.2. Preservation in storage conditions

Light, oxygen, airborne pollutants, moisture, temperature – preservation of plastics requires all of these factors to be kept in check. Besides external environmental influences, reactions to the molecular structure within the material can also cause damage. No single firm set of preservation rules can be determined for plastic items. These are a very diverse group of materials, which all require a different approach, depending on the polymer, additives, size of the item, damage and condition. And we can only dream of separate storage facilities that are made specifically for plastic. The reality is that plastic will be stored together with other materials, in which case it is essential to find a happy medium – preservation conditions suitable for all the materials that are stored together.

5.2.1. Light

Museum vaults are generally dark, windowless rooms, so there is no concern about UV radiation. But artificial light can pose problems. If fluorescents/daylight bulbs are installed in the vaults, they should be covered with filter film. Fluorescents lamps emit a significant amount of UV light. Filter films can be ordered as sleeves or sheets and completely block UV radiation

If the vault has windows, they should be covered. Again, UV filter film is recommended and should be applied to the insides of the windows (there are also films meant for the outside of the pane). Window films are laminated polyester materials whose layers are modified with substances – generally carbon or aluminium particles – that absorb, diffuse or reflect UV radiation and visible light. The exterior of the film is reflective due to the particles. Another option for protective films has embedded organic molecules that absorb UV radiation. Protective films last about 10–15 years.[165]

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[165] Springer 2008.

5.2.2. Temperature

The air temperature in the storage facility should not exceed room temperature (21–23 °C). Naturally, a cooler room (< 15 °C) would be better. Reducing the temperature by 5–10 °C halves the rate of chemical degradation (plasticiser migration, oxidation, hydrolysis). A suitable storage temperature for PVC-P and cellulose esters is < 10 °C. If a PVC-P item is placed inside an ordinary home freezer, plasticiser migration slows down more than tenfold.[166] If a decision is made to store museum items in cold conditions, attention should be paid to any temperature fluctuations. They can prove very hazardous. Plastics shrink and harden in the cold and expand and soften as they warm up. For example, a copper pipe will shrink by 0.01% with a drop of 10 °C. Under the same conditions, an HDPE pipe will shrink by 0.07%, PP and PVC-U by 0.04%. Expansion and contraction is particularly dangerous when items are made up of multiple types of plastic. In this case, the different materials expand and contract in differing amounts, causing mechanical damage. More on the freezing of plastics is discussed later.

If the vault has windows, objects should be kept away from them. Glass does not maintain a stable temperature – it radiates cold at night and heat on sunny summer days. Attention should also be paid to radiators and cold-water pipes. Although the vault's temperature may be within normal limits, this may not be the case near a heating element. Note: refrigerators also give off heat.

5.2.3. Relative humidity

Relative humidity, abbreviated RH, is a measure of the water content in air at specific temperatures expressed as a percentage of the maximum amount of water vapour the air can hold at that temperature. The cooler the air, the less water it can hold. For that reason, air temperature should always be given as well when specifying the relative humidity.

For a storage facility kept at 18–22 °C, a good relative humidity is between 35–45%. Exceptions are celluloid, cellulose acetate and ebonite, which are sensitive to moisture, and in these cases RH should be 30–40%. On the other hand, casein and some nylons are hydrophilic. Water is a plasticiser for casein formaldehyde and the plastic contracts in excessively dry conditions. Because of this, the RH for storing hydrophilic plastics can be over 50% but certainly not over 65%, due to the risk of increased microbial activity. Low RH runs the additional risk of plastics becoming electrostatic and attracting dust.[167] Sudden fluctuations in moisture levels are very hazardous primarily for hydrophilic plastics and plastics that contain absorbent fillers (e.g. phenol formaldehyde and urea formaldehyde). Sudden swelling followed by contraction can cause material to crack. Microcracks from humidity fluctuation have even been observed in PMMA.[168]

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[166] Shashoua 2014: 13–15.

[167] Rivers, Umney 2003: 330.

[168] Lagana, van Oosten 2011.

Indoor humidity levels must be consistently regulated. To reduce moisture in airtight storage containers and sealed cases, a common desiccant used in packaging and as kitty litter – silica gel – can be used. “Gel” may sound like viscous but it is actually a granular, porous crystalline material. It is a reusable, very good moisture-absorbing material, similar to a rigid sponge. It can be used to stabilise the microclimate. Bear in mind that silica gel only works in an airtight micro-environment. If air from outside gets in, a constant moisture level cannot be maintained.

5.2.3.1. Uses of silica gel

Silica gel comes in both milky translucent varieties and ones containing indicator pigments. There are two types of the latter: some change from blue to pink at about 40% RH, while others turn from orange to dark green. Indicator gels are much more expensive, and so it is a good idea to use a mix of indicator gels and ordinary silica gel.

Ordinary silica gel next to silica gel containing indicator dye. Photograph: Anu Ansu and Berta Jänes

The quantity of gel granules depends on whether the item is hydrophobic; the desired RH; the difference in RH between the sealed environment and surrounding space; the size and airtightness of the container; the stability of room temperature and the necessary duration of the microclimate being established. Generally, a suitable amount is ~0.8–1.6 kg per 0.1 m^3 of space. The easiest way of deploying silica gel in a microclimate is to scatter it on a tray with higher edges. If pouches are needed for the silica gel, they should be made of polyester, nylon or polypropylene textile. Most importantly, the material should be permeable and not too thick. The items and the silica gel must not come into contact with one another. Granules should be scattered in the container in a well-ventilated room or outdoors, in fresh air. Be sure to wear a dust mask and latex or nitrile gloves. The dust can cause respiratory ailments and long-term lung damage.

Before using silica gel, it needs to be prepared by introducing the suitable amount of moisture, either through drying or wetting. Moisture content can be determined by weighing the silica gel itself or the RH measurement. When weighing, a certain quantity of granules should be weighed and the result compared with the silica gel’s standard weight. The moisture content of silica gel can be measured with a calibrated hygrometer, taking about half a cup of crystals and placing them into an airtight container (such as a jar). Be sure that the hygrometer does not touch the silica gel. After two hours, the measuring device should yield a result.[169]

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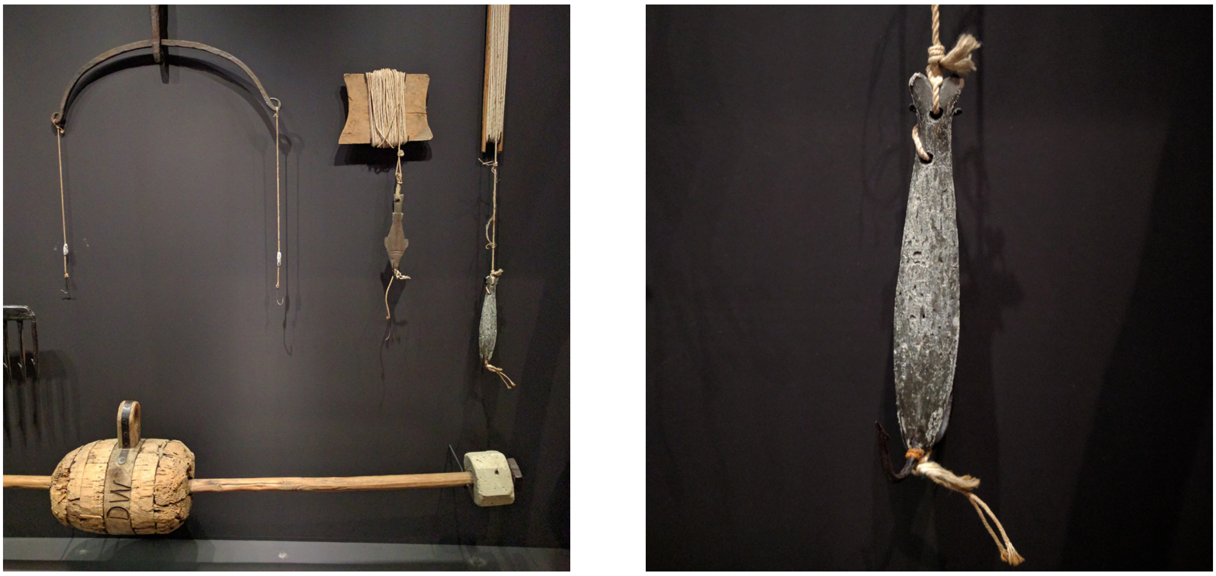
[169] Weintraub 2002.

There are several ways to reduce the moisture level of silica gels. The granules should be placed on a tray in a layer no more than 1.5 cm thick and heated in an ordinary oven at 65 °C. Temperature and time may vary depending on the silica's moisture level, the desired RH and the type of gel used (it could take several hours to achieve the desired result). Indicator granules must not be heated over 120 °C, and ordinary granules not over 200 °C. The gel can also be dried in a microwave and in this case, a 1.5 cm thick silica gel layer should be scattered on a glass pan and heated on high for a minute or two. Then the granules should be cooled, stirred and reheated until the material is dry. To raise the moisture level, the granules should be spread out evenly across a flat surface which is then placed inside a plastic bag or some other container. Then a wet sponge or container of water should be put inside the bag or container. Do not pour water directly onto the silica gel.[170]

5.2.4. Contaminants and ventilation

Contaminants may enter storage rooms in several ways. One possibility is outside air containing many harmful substances entering through the ventilation systems. Within an interior, hazardous gases may be released from furnishings, finishing or construction materials. For example, MDF (medium-density fibreboard), which is widely used for making display cases, releases formaldehyde, which then corrodes metals and damages paper and plastic. Museum items also contaminate the air as they age. For example, woollen items and natural vulcanised rubber give off sulphur compounds, which harm not only plastics but copper and silver.[171] As mentioned earlier, many plastics start releasing acidic compounds as they age – the most unstable ones are nitrocellulose, cellulose acetate and PVC-P.[172]



Hooks made of tin on display at the National Museum's Finno-Ugric permanent exhibition Echo of the Urals became coated with a layer of corrosion in less than six months. Closer inspection revealed debris from corrosion that had crumbled off the hooks. It was caused by off-gassing of formaldehyde from MDF boards used in the structure of the display case and by poor ventilation within the cases. Photographs by the author

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[170] Bennett 1999.
[171] Thickett, Lee 2004.
[172] Hatchfield 2004.

The following table[173] shows materials that may give off volatile organic compounds or VOCs:

Material	Examples of products	Substances released	Materials damaged
Wool	Fabrics, felt, carpeting, skirts, jackets, belts, gloves, socks, etc.	**Compounds containing sulphur:** **hydrogen sulphide H_2S** **carbonyl sulphide COS**	Silver, copper, plastics.
Natural rubber	Adhesives, various items	**Compounds containing sulphur:** **hydrogen sulphide H_2S** **carbonyl sulphide COS**	Silver, copper, plastics.
Wood, wood chipboards	All woods, especially oak and chestnut; MDF, plywood, OSB, other wood fibre-boards, cardboard, particleboard	**Organic acids:** **formic acid HCOOH** **acetic acid CH_3COOH** **formaldehyde CH_2O**	Lead, copper, zinc, cadmium, magnesium, ceramics, stone, seashells, paper, plastics.
Paints, adhesives, varnishes, sealants, anti-fungals	Oil-based, polyvinyl acetate, polyurethane content, some silicones	**Organic acids:** **formic acid HCOOH** **acetic acid CH_3COOH**	Lead, copper, zinc, cadmium, magnesium, ceramics, stone, seashells, paper, plastics. All materials are vulnerable.
Adhesives, paints	Urea and phenol resins	**formaldehyde CH_2O**	
Plastics	PVC, PVDC	**chlorine compounds**	Copper, aluminium, zinc, iron.
	Nitrocellulose	**nitric acid HNO_3.**	Almost all materials.
	Cellulose acetate	**acetic acid CH_3COOH**	Almost all materials.
	Polyurethane	**nitrogen compounds**	
	Polystyrene	**styrene**	

5.2.5. Controlling materials that release acidic substances

Both from the standpoint of the object and the surrounding museum pieces, it is important to ascertain whether any of the items or surrounding materials give off volatile organic compounds. If that is the case, follow-up preservation measures can be taken, such as modifying ventilation systems, using absorbents, or removing the hazardous items. Analytical methods provide precise results: take a sample of the indoor air using a mechanical pump and study it with analytical equipment. There are three options for performing investigations outside the lab: a cresol red test, acid detection (AD) strips, or metal coupons.

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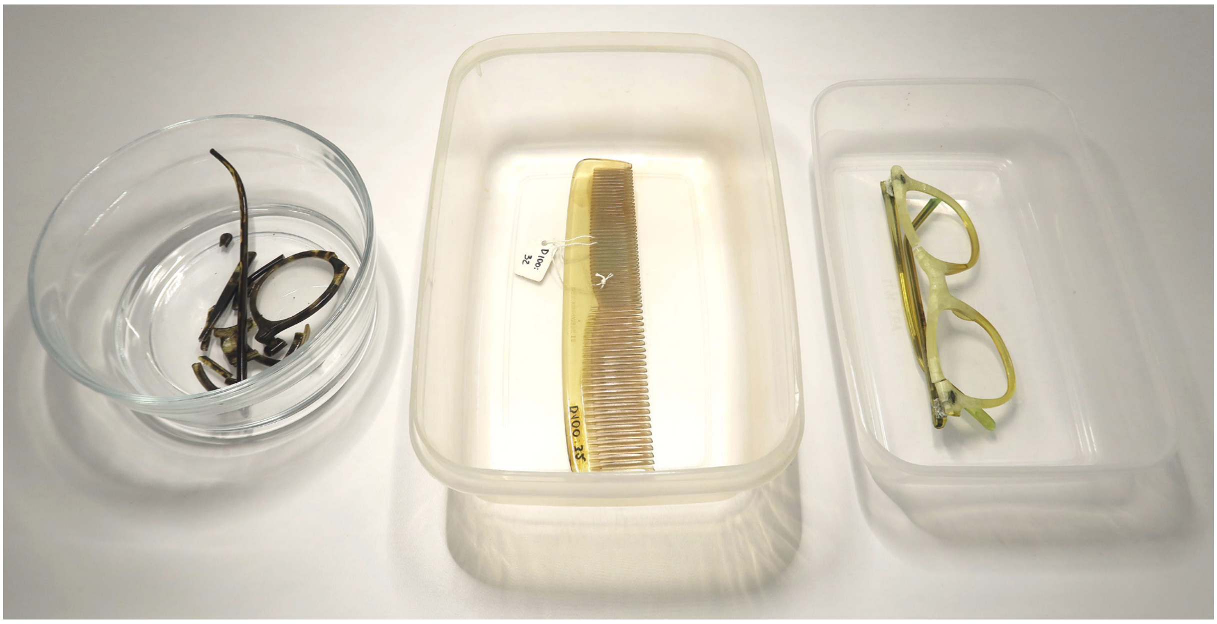
[173] Thickett, Lee 2004.

5.2.5.1. Cresol red test

Cresol red helps to determine whether a nitrocellulose item gives off acidic substances. The experiment needs a piece of cotton fabric to be dipped in a cresol red–impregnated aqueous solution (cheesecloth is a good choice). The solution is made based on the necessary quantity using 0.4 g of cresol red per 100 ml of water.[174] Once excess solution has been wrung out of the cheesecloth, it should be allowed to dry, preferably in a drying cabinet, since cresol red is very pungent. It is recommended that a dust mask be worn, as cresol red paper is very dusty. Wear a smock or other protective work clothing.

The object to be tested is then placed in an open glass or plastic box (PP or PE) which is covered with the cresol solution-soaked cheesecloth. The cheesecloth should not be overly crumpled, otherwise cresol red pigments could stain the item. For that reason, the cheesecloth-covered box should not be moved around too much. If the test is positive, nitric acid is formed and a reddish stain appears on the cheesecloth. In general, you should wait at least 48 hours for the test to yield results. If the item releases a particularly large amount of acid, the colour change will occur much sooner (as little as a few hours). The faster the reddish stain appears on the cloth, the more extensive the activation of the material's chemical degradation.



Objects made of nitrocellulose prepared for the cresol red test. Photograph by the author

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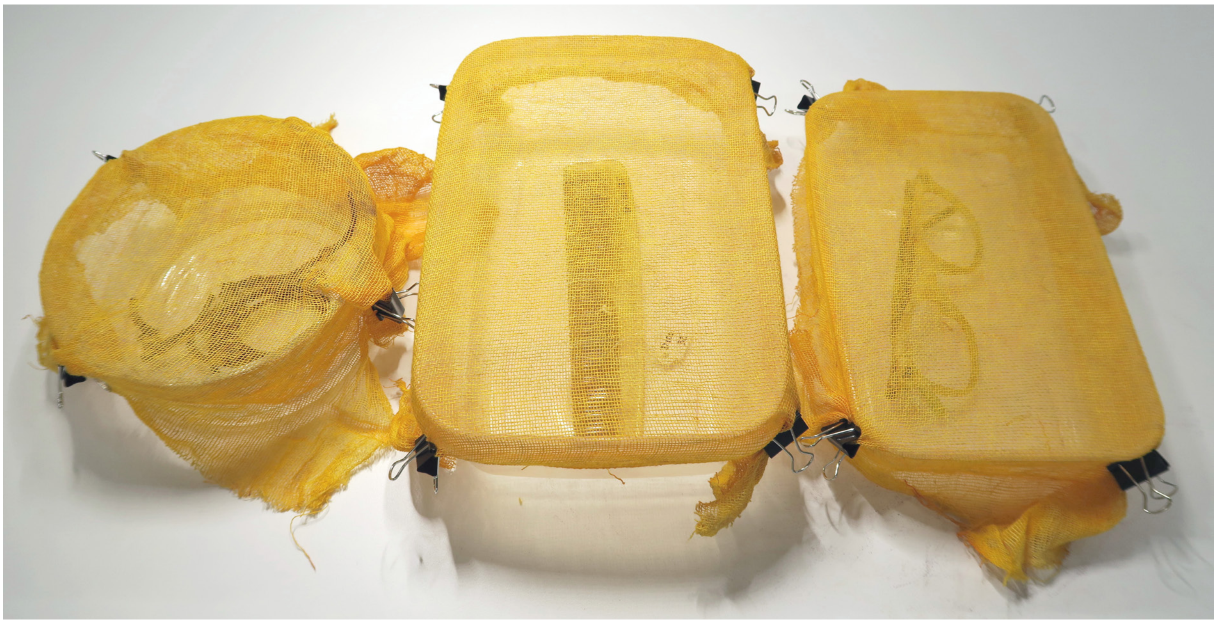
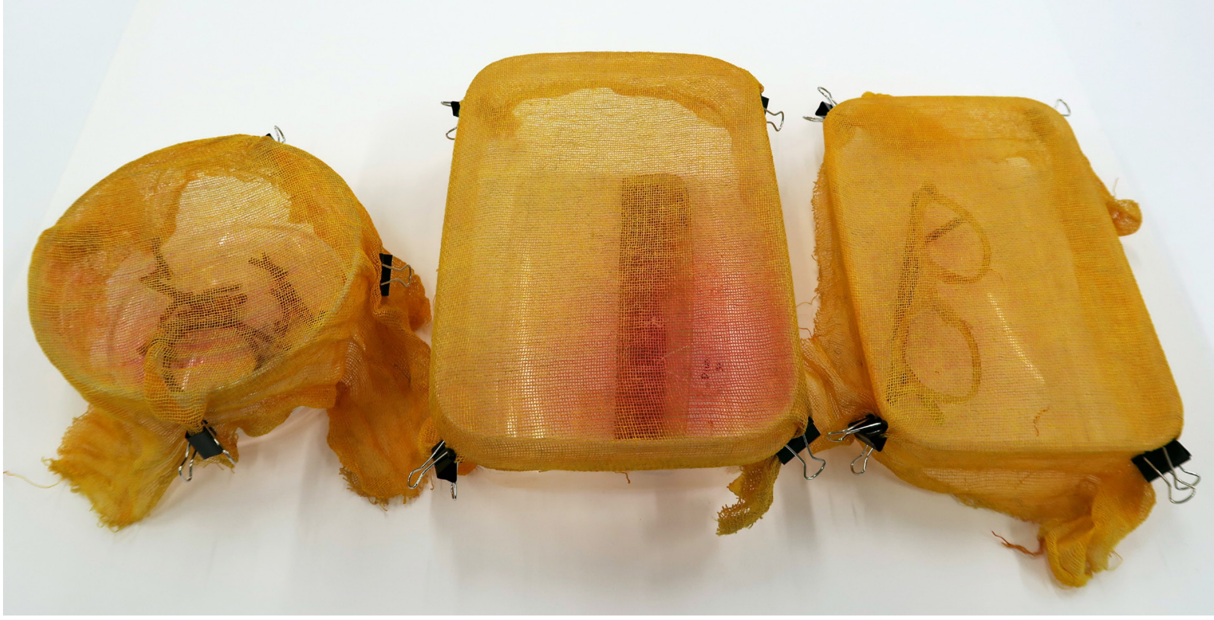
[174] Odegaard, Carroll, Zimmt 2005: 186–187.



Nitrocellulose objects are covered with cheesecloth impregnated with an aqueous cresol red solution for the test. Photograph by the author



The reacted cresol red indicates that nitric acid is being released from the objects. Photograph by the author

Cresol red can also be used to make nitric acid indicator papers. To prepare a cresol red solution, combine 10 ml of methanol, 90 ml of ethanol, and 0.005 g of cresol red. Dip test paper strips into the solution and dry them. Then place the test strip in the proximity of the object being tested (but not touching it!). Examine the strip for colour change, which usually takes place within one or two days. If acidic compounds are present, the paper goes from yellowish to reddish pink. New nitrocellulose materials do not give off acidic substances, and so do not test positive. Older items that are actively ageing may turn the test strip completely purple.[175]

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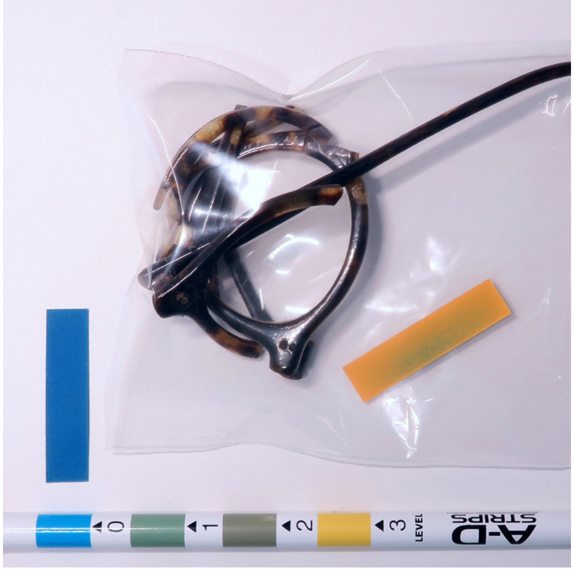
[175] Odegaard, Carroll, Zimmt 2005: 186–187.

5.2.5.2. Acid detecting strips

AD-strips (short for acid detection strips) are indicator papers that change from blue to yellow when they react with a volatile acid. The more yellow the colour, and the faster the strip changes colour, the more acidic volatile organic compounds are present. AD-strips were developed for testing cellulose acetate films, but in addition to acetic acid, they also show the existence of other acidic substances (such as nitric acid and sulphuric acid compounds). AD-strips are meant for short-term use.[176]

To measure, the plastic object is placed in a sealed environment (such as a polyethylene Ziploc bag) together with the AD-strip, which may not directly touch the object. Then the observation starts. If the item releases a particularly large amount of acid, the colour change may be noticed in as little as a few hours. If the indicator strip has turned green or yellow, it is certain that the object is releasing an extensive amount of acids. The item should be monitored for at least a week, because it can take more time for some objects to give off acids. The used strip should then be compared to a control scale and the result recorded. The data should be recorded immediately. If the test strip is in an open environment, its colour will change quickly and the result will no longer be accurate. AD-strips are meant for single use. Detector strips are light-sensitive and must be stored in the dark.[177]



The accompanying photo shows an acid detection test conducted on celluloid eyeglass frames. The photo was taken after 48 hours had elapsed. The item is clearly giving off acidic compounds. Photograph by the author

5.2.5.3. Metal coupons

The existence of volatile organic compounds released by materials can be detected by using metal coupons. The test can also be conducted to detect air pollution within a display case. This method is good for longer term experiments, as metal coupons react with acidic compounds more slowly than AD-strips. They can also be used without isolating the object. Silver, lead and copper are the most common metals used for this test.

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[176] Goughlin 2011.
[177] Goughlin 2011.

Special metal sheets are needed for this test, which are at least 99.5% pure and 0.1 mm thick. After being cut to suitable sizes, they must then be carefully cleaned (e.g. using acetone). After cleaning, they may be handled only with tweezers, not by hand. Metal coupons may not come into direct contact with the objects. Initially, the process is monitored weekly. If no changes are noticed, the process can be monitored once a month. The metal sheet reactions must be documented and recorded. Silver becomes coated with a dark grey layer in the presence of sulphides, lead becomes greyish white in the presence of organic acids or aldehydes, and copper becomes green, brown or black when reacting with chlorides, oxides or sulphur compounds.[178]

Metal coupons placed in the National Museum's Echo of the Urals exhibition display case. The lead sample became light-grey in a few months, showing that there is a ventilation problem – the aldehyde concentration inside the case is too high. The copper sample has not experienced change, showing that the concentration of chlorides, oxides and sulphur compounds is not excessive. Photograph by the author

5.2.6. Scavengers

If the items in storage are known to emit volatile organic compounds that accelerate ageing, or if the air in the storage room contains compounds that are undesirable for various reasons, they can be kept under control with special absorbent materials and systems. We can use absorbent filters in the room's ventilation system, or also create micro-environments for objects that require special attention.

5.2.6.1. Oxygen and Ageless®

Reducing the oxygen level is important for natural rubber objects. In their case, oxidation is the main ageing process, and ultimately makes the material extremely brittle. Reducing oxygen in an airtight package is actually nothing unusual. It is used quite extensively in the food industry. Anyone who has bought a package of beef jerky is probably familiar with the packet marked "Do not eat". Perhaps you have opened the packet and seen the brown powder inside it. These are oxygen scavengers developed by the Mitsubishi Gas Chemical Company, marketed as Ageless®. Specially processed iron powder oxidises in the presence of oxygen and forms ferric oxide. In a properly sealed environment, Ageless pads can absorb nearly all of the oxygen sealed in the package. Besides preventing oxidation, an oxygen-poor environment halts microbial and insect activity.[179]

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178 Goughlin 2011.
179 Daniel, Lambert 1993.

Mitsubishi manufactures different types of Ageless packets. For example, there is a particular variation for packaging products with a high moisture content – Ageless FX starts reacting with oxygen only if the relative humidity is sufficiently high (> 65%). The other products (Ageless S, ZP, ZTP, E) already contain water to enable the reaction. Ageless SS packets are used for freezing, and Ageless SA is for cool storage (although other packets also work in sub-zero temperatures, their absorption capacity decreases as the temperature decreases). There are even some oxygen scavenger options that use organic compounds instead of iron powder, for example vitamin C. These are called Ageless GLS and GE, the latter one simultaneously producing carbon dioxide as it reacts with oxygen, which prevents package shrinkage caused by oxygen loss.[180]

Ageless's absorption capacity is specified by how many millilitres of oxygen one small packet is able to absorb. For example, Ageless ZPT 1000 is able to absorb up to 1000 ml of oxygen. As the atmosphere is about 1/5 oxygen, one packet can remove the oxygen from 5 litres of air. Ageless comes in absorptive capacities of 20 ml to 2000 ml. Packets should be replaced every five years, as there is inevitably some sort of influx of air and sooner or later the absorbent will be depleted.[181]

Suitable film material and a soldering machine are required for airtight packaging of items. There are a number of films available, both opaque and transparent. A transparent one produced by Mitsubishi Gas Chemical Company is called Escal®. This is a three-ply laminate, the outermost layer of which is a durable plastic with a high melting point (polyester, polyamide or polypropylene). The middle layer is a dispersion of ceramic material. This is the barrier that is impermeable to gases. The innermost layer is polyethylene that melts at a lower temperature. Escal® can be heat-sealed at 117 °C. In silver barrier films (such as Marvelseal®), the outermost layers are the same as for Escal® described above, but the barrier layer is made of a dispersion of metal particles. As transparent barrier films are more expensive, the two films can be used together.[182]

An example of an oxygen-free preservation method. A silvery opaque film (Marvelseal) and a special gas-impermeable film (Escal) were used. In addition to the Ageless packet, an Ageless Eye was also placed inside the packaging. Photograph by the author

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[180] Mitsubishi Gas Chemical Company.

[181] Dyer and others 2011.

[182] Brennan 2008: 747–750.

Note that when used in a properly sealed package, Ageless will reduce the amount of air in the container by up to 20%. The shrinking packaging can damage the item. More fragile items can be placed in a vented plastic box and only then into airtight packaging. Special polyethylene foam supports can also be made. Once placed in the container, the Ageless pads must not touch the item. Under normal conditions, the temperature of Ageless packets is 46 °C. In containers, they should always be kept apart from each other to prevent local temperature rise.[183]

Ageless pads should not be used to preserve actively ageing semi-synthetic plastics (casein formaldehyde, nitrocellulose or cellulose acetate). The iron oxidation reaction gives off a certain amount of moisture and heat. Instead of slowing the degradation, the moisture may end up causing the opposite. PVC-P is another plastic that should not be placed in an airtight container with Ageless. It tends to promote plasticiser migration.[184] Unused Ageless pads should be packaged in airtight vacuum packaging, since while they are in the open, they start reacting with the ambient oxygen. This makes it impossible to be sure that the pad still has enough capacity to remove all of the oxygen from the package.

Yet another product, called Ageless Eye, can be used to check the oxygen level in the microenvironment. This is a small packet that contains an indicator dye that turns from purple to pink when the oxygen level falls below 0.5%. If the oxygen level rises, the packet returns to the purple colour. These packets can be reused for a certain period, although the colour change will not occur as rapidly. Ageless Eye must be stored in a dark, anaerobic environment, in cool conditions (< 15 °C). Each Ageless Eye is separately packaged in an air-permeable cellophane envelope. This envelope does not need to be opened.

Ageless Eye is not a completely reliable and durable measuring instrument. Consequently, several indicators should be used in a single enclosed environment. It may take several days for the indicator to change colour. Once it has turned pink, the date on which the change occurred should be recorded on the outside of the environment.

5.2.6.2. Acid scavengers

A number of products are available for binding volatile acidic compounds given off by items or found in the storage environment. Activated charcoal (in the form of textile, sheets or granules) is used in gas masks and the exhaust hoods over stoves where it absorbs food odours. Activated charcoal has been used in conservation since the 1990s for slowing the degradation of cellulose plastics, because it absorbs organic acids. Using a sheet of activated charcoal textile as a filter on a ventilation system will absorb 90% of the volatile nitric acid and 95% of the volatile sulphur dioxide. Carbon sheets and fabrics must be replaced regularly and often, because it is not possible to tell when its activity level declines.[185]

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[183] Burke 1996.

[184] Ledoux 2014.

[185] Shashoua 2014: 13–15.

Preservation Equipment Ltd. (PEL) markets a specially patented microclimate filtration material to absorb harmful gases in indoor areas. The filter textile is meant for use in display cases and preservation containers. It is capable of removing sulphur dioxide, nitrogen oxides, ozone, acetic acid, nitric acid, formic acid, formaldehyde and other organic substances that could prove harmful to museum items. Note that it does not affect relative humidity in the microclimate. A sheet of the material in the appropriate size must be placed in the display case or storage container as close as possible to the item/material that is releasing the harmful substances. Since it is hard to determine exactly when the filter material is depleted, the filters need to be replaced every 2–3 years. Unused material must be preserved in airtight packaging, protected from light.[186]

A test for determining the suitable size of a textile filter. The photograph was taken after 48 hours had elapsed. Although the sample was not large enough, the filter does clearly work when the test result is compared to a control where a charcoal filter was not used

Zeolites, which are highly porous synthetic crystals with specific pore sizes, are used to bind nitric acid. They were first used back in 1994 for preserving film negatives made of nitrocellulose. Zeolites also bind water molecules, thus reducing the chance of hydrolysis.[187] Interestingly, the silica gel used to keep relative humidity under control, described in a previous section, also absorbs aldehydes and acetic acid. It is a good option for airtight display cases with problems due to the release of aldehydes from construction materials, or for storage of cellulose acetate items.[188]

5.2.7. Packaging plastic items for storage

It is important to be aware of which types of items are stored together. Ideally, all plastic types should be housed separately. Plastic should definitely not be placed next to metal (silver and copper in particular), wood (especially oak) or tanned leather. If an item consists of materials that react with each other (e.g. a knife with a cellulose acetate handle or a leather belt with a galalith buckle), they should be separated from one another with a layer of material. The metal parts should be covered with polyester film (such as Mylar®), whereas the plastic should remain exposed. Museum items should not be heaped into the same box – 2/3 of the volume should remain empty. Nor should boxes

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[186] PEL, Microclimate Filtration.
[187] Shashoua 2008: 196–197.
[188] Shashoua 2014: 13–15.

be stacked. This only means needless moving, if an item is needed from a lower box. Large-scale plastic items can be covered with Tyvek® textile, which lets air through and blocks exposure to dust and light. In some situations, vacuum bags that block oxygen can be used (e.g. Cryovac BDF-200, Marvelseal®).[189]

5.2.7.1. Buffered or unbuffered cardboard?

There is some confusion as to whether buffered or unbuffered cardboard should be used for storage containers. Starting from the 1850s, instead of linen or cotton rags, paper began to be produced from wood fibres, which contain lignin. But lignin becomes acidic over time. Besides the paper, the acids also damage items exposed to the paper.

The acidic components can be removed chemically, but then, the chemical compounds that are to some extent inevitably left in the paper (such as bleaching agents), may degrade over time and also become acidic. During manufacturing, alkaline substances such as calcium carbonate or magnesium carbonate are added to buffered paper and these moderate the paper's pH. The pH of a buffered cardboard box can be between 8.5 and 9.5. Over time however, the alkaline buffer becomes depleted. Therefore, the recommendation is to use unbuffered cardboard and paper, which are neutral or mildly alkaline products (pH of 7 to 7.5) and do not contain lignin. But plastic items that give off acidic substances (such as cellulose esters) should be placed in a buffered cardboard box.[190]

5.2.7.2. Packaging museum items that release acidic substances

If the tests described above reveal that an object made of nitrocellulose or cellulose acetate gives off acidic substances, a customised approach to packaging should be taken. Obviously, a museum piece that releases acids cannot be stored openly among other items. Nor should it be sealed in an airtight container as the acid will start “eating” away the item from the outside. We need something that allows the item to breathe, but keeps the acidic substances from spreading.

The problem can be solved with archive-quality buffered cardboard, tissue paper and PEL microclimate filtration material that absorbs acidic VOCs. Cardboard can even be used to construct a box of the suitable size with a lid that closes (without using adhesives!). The filter cloth must be cut into a size slightly smaller than the box lid. Textiles containing activated charcoal granules may start crumbling from incisions, and thus it is wise to wrap it with tissue paper and fasten to the lid. So now we have a system that allows the item to breathe, but keeps the acidic substances from spreading. An item packaged in this manner can be kept in the same drawer/shelf as other items.

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[189] Quye 1999: 106.

[190] Kilby 1995.

It is advisable to label the box with a warning that it contains an acidic item and should not be opened without good reason. It is also a good idea to affix a photograph of the item to the box. Every six months, an AD-strip should be placed in the box to check whether the system is working. The carbon filter cloth should be replaced about every 2–3 years.

Packaging of acidic items. Photographs by the author

5.2.8. Labelling museum collection items

Marking plastic items is a topic that brings up many questions. If ink or waterproof marker is used to write directly on to the item, the ink is highly likely to seep into the material and spread. The solvent in the marker ink may cause solvent damage to the plastic. There is also the problem of removing the marking. Sticky tape and glue should be avoided as they will leave hard-to-remove stains on the surface of the item. An alternative is to use a ribbon to attach paper/textile labels to the exhibit item. This is a non-damaging method and poses no problems if the marking needs to be changed. As the material ages, labels attached in this manner should be monitored to make sure that any fibres or debris do not get stuck on the surface of the plastic if it has become sticky with age.

But the item's number can nevertheless be marked on such a surface. First, a coat of varnish is applied, making sure the varnish solvent will not react with the plastic in any way. Do not use Paraloid B-72 and acetone solution on polystyrene, PMMA, PVC, nitrocellulose and cellulose acetate, as all of these plastics react with acetone. Water-based Aquazol (10% Aquazol 200 solution in water) is a good primer. Because Aquazol is hydrophilic, and becomes sticky as humidity rises, it should be coated with a second layer of varnish. Paraloid B-67 is a good choice for this. This will now keep the ink from migrating into the plastic, while allowing the marking to be removed in the future.[191]'[192]

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[191] Arslanoglu 2004.

[192] Cumberland, Sullivan 1993.

The inventory number was inscribed on the celluloid comb in ink, to which lacquer was applied. Such an approach might be acceptable, but in this case, the lacquer has aged markedly. A protective coating of lacquer was not applied under the inscribed number, which may make it impossible to remove the marking without causing damage to the item. Photograph: Anu Ansu and Berta Jänes

5.2.9. Arrangement of plastic items in the storage facility

In museums, plastics are often arranged not according to the materials, but based on the topic or era, with other museum pieces. As a result, plastic skis are kept on the same shelf as wooden ones, PVC-P shoes are next to leather shoes, and plastic pails are together with galvanised sheet metal ones. Although plastics do not tolerate wood, leather or metal in their immediate vicinity, collection custodians and conservators are forced to arrange them this way due to space constraints. If at all possible, the “malignant” plastics should at least be kept separate from other items, either in a separate room or a sealed storage container filled with acid scavengers. Plastic items should definitely not be placed into a sealed box/bag together with other materials. It is also advisable to keep different plastics separate from each other. Markings must be made on boxes containing unstable plastic objects to flag them during condition surveys.

If possible, objects should be stored separately from their original packaging. The reason is the possibility that the packaging and the object will start damaging each other as they age. For example, cardboard boxes will become acidic as they age and may damage the packaged plastic inside. At the same time, a number of plastics give off acidic compounds and harm the packaging. Plastics in a sealed metal or film package suffer from poor ventilation. The package may also be of some other type of material, which should be stored in different conditions.

Damaged packaging of a game console (expanded polystyrene). Photograph by the author

Make sure that objects do not touch others, whether they are made of plastic or some other material. Contact can result in the migration of the material’s components, such as transfer of colour pigments. A problem can also arise if items are separated from one

A video game console from the 1990s was stored in its original packaging. Over time, the PVC-P-coated cords deformed the styrofoam. Photograph by the author. ERM A 951:116

another, using unsuitable materials. For example, tissue paper is unsuitable as a divider between PVC document sleeves (see image on page 103). Over time, the paper sticks to the file folders. Inert materials with smooth surfaces are suitable for separating items, for example polyester, polypropylene and polyethylene film or silicone coated paper. Remember that polyethylene is an absorbent material and can speed up plasticiser migration, so polyester film should be used instead with PVC-P.

Oversized plastic items can be stored on wheeled shelves, which makes it easier to move them. Shelves should not be made of wood or MDF (if they are, they must be varnished/painted with finishing compounds that do not give off volatile organic compounds) and direct contact with metal shelves should be avoided (risk of corrosion). Museum items should be placed in boxes/wrappers made of an inert material to avoid dust buildup and potential damage from light. In some cases, items may need to be reinforced, such as museum items made from expanded plastic with a risk of sagging or breaking in certain places. The supports can be made of polyethylene or polypropylene foam. Another good material is a polyester felt that can be moulded under heat, Fosshape®,[193] which can be easily used to reinforce clothing, for example faux leather garments.

5.2.10. Freezing museum items

Freezing involves placing items in a room where the temperature can drop to –18 °C. A cooler storage environment slows hydrolysis, oxidation and migration of additives and other chemical compounds from materials.[194]

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[193] Turu 2017.

[194] Voellinger, Wagner 2009.

Before acquiring a freezer, it is worth thinking about which items will be kept there and how often access is desired. Special freezers are available, but ordinary home freezers can also be used for storing plastics. A chest freezer (that opens from the top) will accommodate larger items. But a drawback of this type of cold storage is that the items have to be stacked on top of one another. The items on the bottom must tolerate extra weight, and the topmost items have to be moved to retrieve them. A somewhat better solution is an ordinary upright fridge/freezer with several shelves inside that can support the weight of the items. It must be frost-free and self-defrosting. Since refrigerators give off heat, remember that it could raise the general temperature in a storage room.[195]

Photograph from an Estonian National Museum exhibition titled “Vaevatud artefaktid“ (Troubled Artefacts, from autumn 2015). To show how an inappropriate freezing method can damage objects, items were placed in a freezer unpackaged. These are of course items from the sample collection. No actual museum artefacts should ever be frozen in this manner. Photograph: Arp Karm

Refrigeration should not be used for objects made of several different types of plastics or those with additional materials (such as plastic and metal). Every material shrinks in a different way when it is cooled. This stresses the item and as it returns to its room temperature measurements, cracks and more serious structural damage can appear. Moisture and condensation are additional risks when it comes to cooling. Some plastics (e.g. casein formaldehyde, urea formaldehyde and polyamides) are hydrophilic, binding water molecules and creating favourable conditions for hydrolysis.[196]

Be mindful of how items are packed before freezing. The packaging protects the item from condensation that forms during sudden temperature changes, which could freeze and cause mechanical damage to the item in deep-freeze conditions. The packaging is also important for maintaining a specific microclimate around the item, as RH can suddenly fluctuate in a freezer. The item must be double-plastic-bagged. The inner bag must not be gas-permeable. This type of bag can be made from a special multilayered film (polyethylene – metal sheet – polyester), such as Marvelseal®, Dri-Shield® and Static Shield®. The last of these is the preferred option as it is sufficiently transparent to see exactly what was placed in the package. A Ziploc bag made of polyethylene film makes a good outer bag.[197]

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[195] Voellinger, Wagner 2009.
[196] Williams 2002.
[197] Voellinger, Wagner 2009.

The less air left in the package, the better, as the moisture in the air condenses upon cooling. The air left in the bags also increases the volume of the package. For this reason, the bags must be precisely the right size. The moisture content within the item should be taken into consideration and must be gradually lowered by taking the item into a drier room. The item should also be gradually "accustomed" to a cooler temperature,[198] by placing it first in a cooler room, then into a refrigerator and finally the freezer. When freezing materials whose glass transition temperature is lower than room temperature, bear in mind they become fragile when cold. Such materials include polypropylene and polyethylene. Freezing is safe for nitrocellulose, polystyrene and polyesters that have thin walls.[199]

The freezing method is meant above all for items whose condition is critical and which do not need to be used for a longer period. Before handling the frozen item, it should be allowed to come to room temperature gradually (from 8 to 24 hours depending on size). The item should definitely not be removed from the bags before it has thawed.

5.3. Exhibiting plastic items

Plastic items should be exhibited in sealed display cases, which allow the environmental conditions around the item to be kept stable and suitable. Dirt and dust on visitors' clothing and shoes, and dirt and dust in the room itself may otherwise adhere to electrostatic or sticky objects. VOC absorbents can be used in sealed display cases, ensuring stable relative humidity and as a dust barrier.

Builders, curators and designers should consult a conservator when assembling display cases. One essential matter is the choice of materials used to construct the display case. Another subject has to do with which objects can be placed next to each other in the case. Be vigilant about "malignant" plastics (nitrocellulose, cellulose acetate, PVC-P, polyurethane foams, vulcanised rubber), for as they age, they release chemical compounds that harm other items. Thus, it would be wise to display these hazardous plastics separately from other objects, or at least place them further away in the display case. It is advisable to use activated charcoal, which absorbs acidic substances. The damage could also take place in reverse. The sulphur compounds and organic acids given off by woollen materials and wood accelerate the ageing of plastics.

What if a plastic item needs to be displayed out in the open? If it is too large to fit into a showcase, or if it is meant for hanging on a wall, or if it is intended to be touched? For conservators and preservation specialists, this is a headache. Furniture and large sculptures need proper care, including dusting and ensuring that no mechanical or chemical damage has occurred. One thing is clear: plastics can only be exhibited in the

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[198] Ledoux 2014.

[199] Shashoua 2008: 206.

open temporarily. Also, the type of plastic should be considered. If the item is made of a semi-synthetic plastic that is already old and degraded, it should not be displayed openly at all. In some cases, the item can be consolidated with suitable measures, for example, polyurethane foams with antioxidants and light stabilisers. This will be discussed in the next chapter.

Plastic bags displayed in the Estonian National Museum's permanent exhibition Encounters have been placed in a hermetically sealed environment, while the case with the shoes has ventilation openings since the materials (polyurethane, PVC, natural rubber, leather) give off volatile organic compounds that could damage items in an airtight environment. Photograph by the author

5.3.1. Climate and environment

As in the case of storage conditions, a cooler temperature is also better for exhibiting plastics. Understandably, the overall temperature in the exhibition hall must be comfortable for visitors. At room temperature, it has to be taken into account that all sorts of chemical ageing reactions take place faster than in cooler conditions. For this reason, plastic items in a permanent exhibition should be periodically rotated. I know it is a great temptation to not do this. More than a few people have thought: “This item looks just like it did five years ago! Why should I take apart the whole display case and look for a replacement?“ If a plastic item already shows visible signs of ageing, things are pretty dire. No chemical degradation process is reversible (at least not without damaging the item). Once yellowed, the item will stay yellow. A brittle item cannot be made elastic again. Additives that have migrated to the surface cannot be forced to re-link with the polymer chain. Analytical instruments can be used to concretely monitor degradation and the changes in the chemical composition of an ostensibly unchanged plastic item. Sooner or later, plastics age anyway. Our job is to hinder that process for as long as possible.

The moisture level in the display case must be monitored. A high relative humidity poses a risk of mould growth and problems can develop with surprising speed. At a temperature of 20–24 °C, a suitable relative humidity inside the display case is 40–55%.

5.3.2. Keeping volatile organic compounds in check inside display cases

Testing of paint intended for coating display cases at the Estonian National Museum's new permanent exhibitions. After drying for a month, the paint was peeled off using a scalpel. Photograph by the author

Oh, how simple it was back in the days when suitable items were sought out and arranged in an aesthetic composition inside an existing display case! If a suitable exhibition cabinet could not be found, a craftsman was contracted to build the cabinet from materials on hand. If the display case needed to be white on the inside, it was painted white. If the items were to be displayed on a red fabric, that was what was done. There were no exhortations such as "this cannot be paired with that" or "this material gives off VOCs, which speeds up degradation“. Now, however, we know enough to be cautious. If the showcase is not made of glass or acrylic material, it is very likely that the materials used could affect the quality of the air inside the display case.

In autumn of 2016, the Estonian National Museum (ENM) moved to its new location. Several materials were selected to build the display cases for the permanent exhibition, but these set off alarm bells for the conservators: MDF board, plywood, EPS, aldehyde-based paint. Many display cases were designed to be airtight, i.e. everything given off by the materials used for the cases would have accumulated and remained inside the case. An Oddy test[200] showed that MDF and aldehyde paints gave off hazardous compounds. The paint was not a problem, as it could be replaced with water-based acrylic paint. MDF posed a greater problem, as it had been planned as the main construction material. For this kind of material, it is possible to create a barrier layer that prevents the volatile compounds from being released, either with several coats of an inert paint (water-based acrylic paints and lacquers containing calcium carbonate (binds various acidic substances), non-alkyd urethane paints and lacquers) or the installation of barrier film sheets. Since the exhibition had extensive display case surface area, ENM opted for the painting. All surfaces inside the display case had to be painted, even ones that are not visible to visitors, such as the bottoms and backs of the cases. Paint is used primarily as a barrier, and the aesthetic value in such instances is an added plus. As noted, several layers of the paint should be applied. Oil paints contain carboxyl acids, aldehydes and peroxides, due to which they should not be used for coating surfaces inside display cases. Painted/varnished materials should be given enough time to dry (at least four weeks would be good), so that any solvents given off during the drying process do not accumulate in the case.[201]

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[200] Korol 2015.

[201] Tetreault 1999.

Another option is to install barrier film on the MDF or plywood, which has polyethylene on one side and a polyester-coated aluminium sheet on the other (e.g. Marvelseal 360). The film is installed onto the subsurface using an iron or heated spatula. The side coated with polyethylene (slightly more matte) is placed facing down and then melted to the wood with the iron. This results in a silvery surface that should be coated with a neutral fabric or board to protect it against scratches. The coating material should be fastened to the film using double-sided tape or hot glue. Nails and staples will puncture holes into the film, which provides an inlet for organic compounds to find their way into the case. A protective film of this type can be self-made by using polyethylene film and foil. The materials are placed on the wood in layers: film at the very bottom, then foil and then a sheet of paper, so that the iron does not tear the foil during ironing. DIY protective film is even less protected against scratches, and therefore should definitely be coated with protective material. Tears and holes in the foil can be patched with polyethylene film and foil, using the technique described above.[202]

5.3.3. Lighting

Exhibition hall lighting is extremely important. The same also applies to display cases. Light is used to help direct visitors and to highlight the most significant parts of the objects. Light, however, is the main cause of plastic degradation. Whether direct or diffused, sunlight should not be allowed to fall on exhibited items. If an exhibition hall has windows, they should be covered over or special UV-filtering protective films used. It is important to consider the type of artificial light to be used within the display cases and in the exhibition hall. UV radiation weakens the material's molecular structure and damages pigments; while infrared light heats materials and in doing so, speeds up chemical reactions.

There are three options for lighting:

- incandescent bulbs;
- fluorescents;
- LEDs (light emitting diodes).

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[202] Tetreault, Low-Cost Plastic/Aluminium Barrier Foil.

Incandescents, which were phased out in the EU from the autumn of 2012, are very familiar to us – we grew up with them. It was common for the filament to burn out and it was then time to replace the hot bulb. Incandescent bulbs should not be used in display cases as they give off a large amount of heat. Unlike incandescents, fluorescent bulbs do not get as hot. However, they do emit significant amounts of UV radiation. Fortunately, this can be minimised by using filter films. A third option is LEDs. They are currently the most popular choice for lighting the inside of display cases. They do not emit UV or infrared radiation or give off heat. Different intensities and colour temperatures are available. LED lights are also the best option when it comes to energy efficiency, as they use less electricity than other types of lighting and last longer.[203, 204]

Light that falls on plastics should be within the range of 100–150 lux (< 100 lux is recommended). A lux is the unit of illuminance, i.e. luminous flux per square metre. In the evenings, the level of illuminance in living rooms is around 50 lux, while at the office during the day, we are exposed to 400 lux. Direct sunlight is approximately 30,000 lux. It is important to note that illuminance and exposure time are interrelated. For the object, there is little difference between a short period under high-intensity light and a longer period under lower-intensity light – the cumulative light dose is equivalent. In both cases, the resulting light damage is irreversible.[205]

5.4. Suitable materials for preserving and exhibiting plastic museum pieces

As with objects made of other substances, suitable material choices used for preservation, conservation and exhibition of plastic items originate from the item itself and the requirements of the material. The material's physical and chemical properties, texture, air permeability, durability, presence of static charge, length of preservation, quality and appearance should all be taken into consideration. Archive-quality materials are stable and inert and do not release harmful gases that could accelerate the ageing of artefacts. Make sure that plastics containing plasticisers or hazardous additives are not used near the items. Materials containing chlorine or sulphur should also be avoided. It is safe for museum pieces to come into contact with polyethylene, polypropylene, acrylic and polyester film.[206, 207]

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[203] Lindblom Patkus, Protection from light damage.
[204] Conn 2012.
[205] Konsa 2007: 65.
[206] Pasiuk 2004.
[207] Lavédrine 2003: 67.

5.4.1. Oddy test

The Oddy test[208] is named after British Museum conservation scientist Andrew Oddy, who developed the method in 1973. It determines which materials can come safely into contact with museum objects. Many materials give off volatile organic compounds as they age, which can harm more sensitive (e.g. silk, paper) and more chemically reactive materials (silver, copper, plastic). The biggest problem arises when the items are placed into sealed display cases together with unstable materials. Hazardous gaseous substances start accumulating in the sealed environment and damaging the objects in the display case. The Oddy test is a good, relatively simple way of verifying that materials used in conservation, preservation and exhibition are inert.

The Oddy test relies on metal coupons (copper, silver and lead). Each one of them is corroded by volatile organic compounds.

- **Copper** – chlorides, oxides, sulphides
- **Silver** – sulphides
- **Lead** – organic acids, aldehydes, acidic gases

In brief, the experiment takes place as follows:

- metal coupons are placed into an airtight test-tube along with the material being tested and a small quantity of deionised water;
- the test tube is heated at 60 °C for 28 days;
- at the end of the test, the layer of corrosion on the metal coupons is examined and recorded, and the tested material is classified either suitable (S), only suitable for temporary use (up to six months) (T) or not suitable for use (NS).

This is a specific, but rather subjective test. We do not really know how much and exactly what is released during off-gassing. We can only estimate whether the amount released is enough to risk damage to the objects or not. Still, it is one of the simplest tests and museums preparing temporary exhibitions can save money by using cheaper general construction materials instead of costly archive-quality materials.

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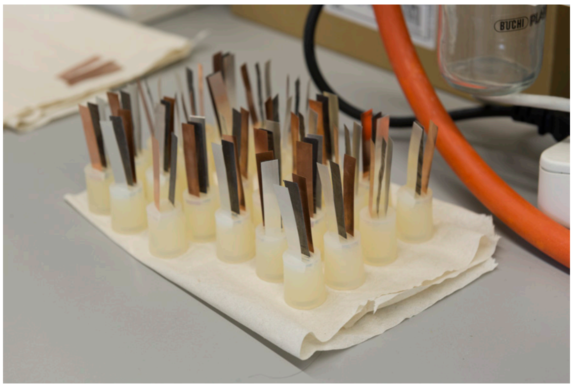
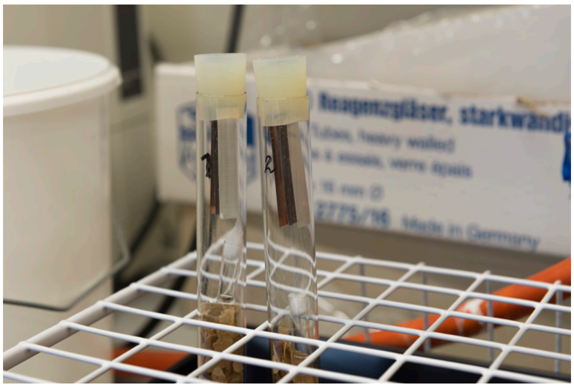
[208] Thickett, Lee 2004.

Samples weighed for testing



Metal coupons prepared for testing



Material sample with metal coupons

Test results. From top to bottom, these are silver, lead and copper samples. Negative control test results are shown in the left column, while the right column shows positive controls and the middle column indicates results for the sample being tested. The test confirmed that the proposed aldehyde-based paint was unsuitable for use in a sealed display case. Photographs: Arp Karm

6.

CONSERVATION

Time heals all wounds, as the saying goes. But when working with ageing plastics, time opens them instead. We can do our best by creating preservation conditions that are close to ideal for the items. If the object is not packaged in a cool, dark vacuum, however, there is little we can do to resist the ravages of time. Little by little, it takes a relentless toll on everyone and everything. Yet a conservator remains stubborn and zealous in defending their treasures from this invisible enemy. Consolidants, adhesives and stabilisers have been developed as “combat” materials, with which it is possible to implement several well-tried strategies – in other words, practical conservation of objects.

The goal of practical conservation is to slow down the ageing of objects through consolidation and essential repairs. Consolidants, adhesives, fillers and surface finishing can be used if they are essential for preserving the item. It is difficult or impossible to remove “repairs” from a plastic item. Thus, practical conservation should abide by the principle that everything done must be reversible and not damage the item in any way. This is particularly important for plastics, because the conservation practices compared to other materials are in their infancy and in reality the wealth of knowledge is fairly scant. Today’s decision may be our downfall in a few years – an adhesive joint could break, varnish can become sticky, and the solvent may cause the material to become more light-sensitive, etc. Because of this, every decision must be carefully weighed beforehand, methods tested, results tracked and most importantly – mistakes learned from.

When choosing conservation materials, it must be taken into account that most commercial adhesives and materials are not suitable for conservation purposes, because their lifespan is too short. Some information is marked on the product packaging, but most details are known only by the manufacturer. This makes the work of the conservator harder, because the precise composition must be known when choosing materials. It is recommended to order conservation supplies from companies that sell archive-quality products. Superglue from the supermarket may appear to serve its purpose, but over time will chemically damage the product. Goods sold by certified conservation material distributors have been tested and are inert. Sellers of archive-quality conservation materials also provide instructions for use, and by following them, there is a greater probability that the end result will be what we were looking for.

6.1. Cleaning

The first part of the conservation process is usually cleaning the museum object. The items acquired by museums tend to be gently or well-used objects or came from someone's private art collection. The first order of business would be to grab a cloth and clean the item. Or even better, pour warm water into a bowl and soak the item. If only things were so easy with plastics. Even wiping can damage the surface of a sturdy plastic item. Damp cleaning is particularly risky, because it can cause moisture damage or strip certain types of finishes. Yes, water is a solvent, too, and it can irreversibly damage items.

A commode (polypropylene) found during field work.
Photograph by the author

6.1.1. Dry cleaning

Dry cleaning refers to removing loose dirt from the item by using a dry cloth, a soft brush, eraser, air pressure or vacuum cleaner. This is the first step in cleaning an item. At the same time as dust is being removed with a brush, it is sucked into a vacuum cleaner with a narrow attachment. When cleaning, use straight, one-directional strokes. Circular motion will cause more damage to the surface and any dirt on the surface may produce scratches. The least damaging materials for plastic are chamois, cotton balls, ostrich feathers, synthetic feathers, eyewear cleaning cloths, sable brush, cotton cloth, microfibre cloth, and pressurised air.[209]

6.1.2. Wet cleaning

If dry wiping does not produce the desired results, continue the process with wet cleaning. Use deionised or distilled water (ordinary tap water can be too hard or contain iron) and special cleaning agents. There is risk involved in this technique, as age-degraded plastics may behave unpredictably in the presence of water, and it is sometimes hard to dry the wet surface due to special surface finishes. Moisture left in cracks or micro-fractures can lead to chemical and physical degradation. Therefore, depending on the item's shape, surface features, dirt, and the extent of it, serious consideration should be given as to whether damp or wet cleaning is a safe approach. Sometimes it is wiser to remove the majority of the dirt from the item by dry wiping it and leave the more stubborn dirt untouched.

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[209] Lavédrine, Fournier, Martin 2012: 234.

A selection of materials used for cleaning plastics. Photograph by the author

The procedure for the PVC-P cleaning test. A 1% aqueous solution of Orvus WA Paste yielded the best result, and 3% triammonium citrate and 96% ethanol also performed passably. Photograph by the author

If cleaning of the item is unavoidable, it needs to be done with caution. It is imperative to know whether the material is moisture-sensitive or not, and again – we have to know what type of plastic we are dealing with. The cleaning cloth used must be barely damp – there should be no drips when squeezed or wrung out. Once the desired area has been cleaned, it needs to be carefully dried.

There are several options for cleaning compounds.[210] Generally, cleaning agents meant for delicate textiles have also been tested on plastics. For example, Orvus WA Paste, which is a neutral pH synthetic anionic cleaning agent, or Sintanol, which is used at the ENM for washing textiles. In some cases, it is a good idea to add a couple of drops of surfactant (such as Surfynol 61) to the water. This may be necessary if the material has a high surface tension (polyethylene, polypropylene). Surfynol 61 lowers the surface tension and evaporates from the surface, without leaving a 'halo'.

6.1.3. Cleaning with solvents

Often surface dirt on plastics cannot be removed with soap and water, such as grease, marker or ink stains. In these instances, solvents come to the rescue. Extreme care should be taken when using solvents for cleaning. It is necessary beforehand to find out what types of solvents can negatively affect the plastic. By choosing the wrong solvent, the conservator can cause irreversible damage to an object. Acetone, for example, is very aggressive toward celluloid. If, due to some confusion, a celluloid surface is cleaned with acetone, damage to the item is inevitable.

Cleaning PVC-P with ethanol. Photograph by the author

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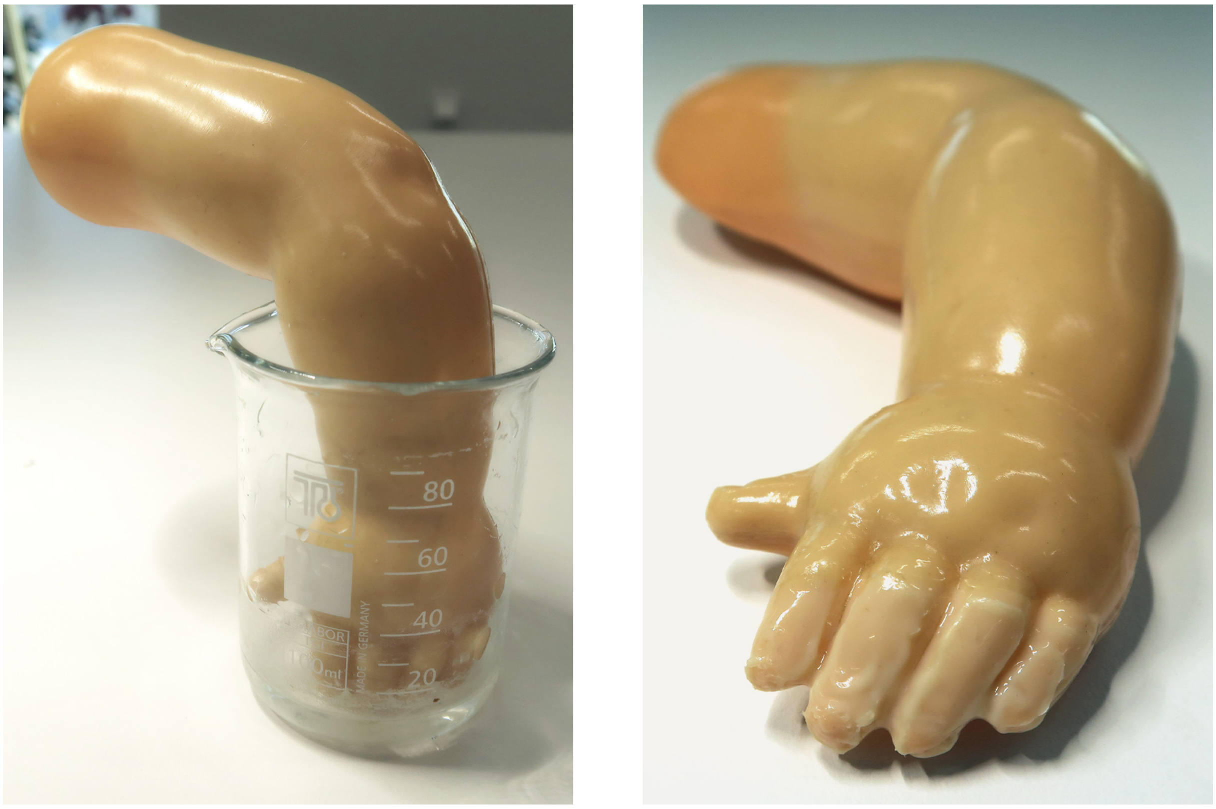
[210] Balcar 2012: 225–252.



The arm of the doll (nitrocellulose) was dipped in acetone for 30 seconds and sustained severe solvent damage.
Photographs by the author

Sometimes the signs of solvent damage take a few days to appear, once the object is already safely on the depository shelves or displayed in the exhibition hall.

The sticky layer of phthalates that migrate to the surface of a plasticised PVC object can be effectively removed with near-pure (95%) ethanol. In addition, it removes surface dirt. Equally, it has to be taken into account that PVC-P still contains a large amount of plasticiser that has not yet migrated. If the storage conditions are not modified, over time it will again accumulate on the material surface. Plasticiser loss makes the plastic more rigid, so frequent cleaning of PVC-P to remove the sticky residue is not advisable. But it is important to clean off surface dirt. In other words, plasticised PVC is absorbent and fine soil on the surface will eventually work its way into the item. At this point, it is no longer possible to clean the item. Soiled PVC-P should therefore be cleaned and attention should then turn to storage conditions.

One of the best aids for the conservator is 95% ethanol. It is safe for most plastics. For example, alcohol can be used to clean mildew spots and other surface dirt off celluloid and casein formaldehyde. It will also remove debris that is stuck to the surface of degraded polyurethane ester.

The PVC-P cleaning test shows how even the best method leaves black specks on the surface. The dirt has "seeped" into the material and can only be removed with more aggressive solvents, such as acetone. Acetone however damages PVC-P surfaces. Photograph by the author

Using ethanol to clean mould from casein formaldehyde buttons. Photograph by the author

6.2. Consolidation

Consolidation – strengthening the material's structure – is used to preserve material that has become fragile and may be crumbling. This procedure is usually irreversible and careful thought should be given as to how or even whether to do it. It is very important to choose an inert material that remains stable for a long period. As little as possible of the consolidant should be used and it should be applied evenly to the material, to ensure equal absorption and to prevent stress at the joints. When selecting a consolidant, it must be taken into account that materials whose glass transition temperature is lower than room temperature will not be able to sufficiently reinforce the item. Their Tg should also be close to that of the material being consolidated, to allow uniform expansion-contraction in the case of any changes to the preservation conditions. The plastics that typically undergo consolidation are expanded plastics and fibres/textiles.

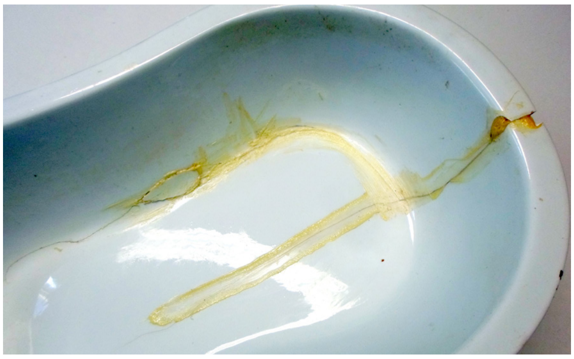
6.2.1. Consolidation of polyurethane foam

Polyurethane foam is one of the plastics that is most vulnerable to harmful agents. Whereas degradation of most plastics usually starts from the surface layers, the open-cell structure of foam material makes it easier for oxygen, moisture and harmful chemical compounds to get in. Therefore, polyurethane foam degrades rapidly and extensively. The colour usually becomes yellower, and then the material starts losing its elasticity and ultimately becomes so crumbly that it collapses under its own weight. Foam rubber reaches this state in just 30–40 years.

Before conducting any consolidation tests, it needs to be determined whether the material is polyurethane ether or ester (see page 82). This is important due to the fact that no suitable method for consolidation of polyurethane ester has yet been developed. Only polyurethane ether can be consolidated with polymers. There are three reinforcing methods available: replacing the air in the plastic with fillers, applying a thin layer of film to the surface, or coating the "cell walls" with a consolidating agent. The result of the first two methods is a hard, inflexible layer that makes the material rigid. Both natural and synthetic consolidants can be used, such as isinglass, gelatine and methyl cellulose or Plextol B-500® (acrylics) and Impranil® (a dispersion of polyurethane in water).

Acrylic resins dissolve in ethanol, acetone, ethyl acetate and therefore work well with urethane groups. Once the solvent evaporates, the acrylic solution forms a thin film layer in the foam's cellular structure, which protects the foam from harmful agents. The glass transition temperature of Paraloid B-72 is 40 °C, which makes it quite sturdy at room temperature. A 10% solution of Paraloid B-72 can be applied to the object using a spray bottle. Acetone, ethanol and ethyl acetate can be used as a solvent. Polyurethane foam treated with 10% Paraloid B-72 remains soft, while the polymer turns hard if 20% solution is used.[211]

6.3. Gluing plastics



Polyurethane adhesive was used to glue together a ceramic bidet. As we see, it has become yellowed. Photograph by the author

Using glue for conserving a plastic item is always risky. Glues can age more quickly than the object, and become brittle, sticky or yellowish. The solvents in the adhesives can damage the polymer and removal of aged adhesives often proves complicated or even impossible. With all of the above risks, it is only justified if the item no longer has its original shape or purpose, or if the damage can cause further problems if it is not fixed. The adhesive chosen must be inert in regard to the surface of the item and it must be possible to remove it later on, either chemically or mechanically.

In restoration practice, thermoplastics can be joined together with a welding technique similar to that used when they were originally manufactured. This kind of joint is nearly as strong as the plastic itself. The plastic itself can be used, or a spare piece of the same plastic can be melted to make the join. Welding is used for example in producing polyethylene bags. A similar join can also be produced by using solvents. Suitable solvents are those with similar solubility parameters to the bridgeable plastic (see Appendix 8, page 201). For example, celluloid can be easily "glued" with acetone. It should be borne in mind that joints and seams made this way are never completely reversible, as material loss takes place during the course of the solvent bonding.

The next sections provide examples of how different plastics can be glued together. Separate coverage is given to joining transparent plastics.

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[211] Chaumat and others 2012: 271–293.

6.3.1. Gluing transparent plastics

Gluing transparent plastics is a more complicated task than it may seem. Not that rejoining the pieces is the insurmountable challenge here. The tricky part is joining the two pieces so that the “X” made by the glue does not stay visible, and to prevent the glue from becoming cloudy or yellowish or even worse – somehow damaging the plastic.

Although it may seem that transparent plastics are just as see-through as glass, their transparency is actually a little different. The difference is shown by using the refractive index (RI). Put simply, the RI shows how much light entering the material refracts when colliding with its constitutive particles.[212]

Plastics and glues have their own specific refractive indices. For an adhesive join to remain unnoticed, the indicators should be as similar as possible (a difference of $< n = 0.02$ between indexes means it is invisible to the naked eye).[213] The refractive indices of glues can be fine-tuned within certain limits. Having found a glue with a suitable refractive index, its chemical stability should also be considered. A number of glues can at first leave an imperceptible join, but after a few years they become yellowish. That is what Paraloid B-72 does. Experiments have shown that epoxy glue HXTAL-NYL-1 and acrylic glue Acrifix 116 withstand yellowing the best.[214]

The following is a table showing the RI values of the most common transparent plastics and the most widely used glues[215] (table also included in the appendix, page 202).

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[212] O’Connor 2015.

[213] Lagana, van Oosten 2011.

[214] Winther and others 2013.

[215] The figures in the table come from the following sources: Scientific Polymer Products Inc; O’Connor 2015; Lagana, van Oosten 2011; CAMEO; Professional Plastics; Rubin 1990.

Refractive index values for the most common plastics and glues

Polymer	Refractive index (n)	Adhesive	Refractive index (n)
Glass (silicone dioxide)	1.46	so-called superglue (cyanoacrylate)	1.45–1.48
Cellulose acetate (CA)	1.48	Polyvinyl acetate (PVA)	1.47
Polymethyl methacrylate (PMMA)	1.48	Polyethylene vinyl acetate (EVA)	1.47–1.48
Polypropylene (PP)	1.49	Araldite Rapid	1.47–1.48
Low-density polyethylene (LDPE)	1.51	Paraloid B-67 (isobutyl methacrylate, 40% solution in mineral solvent)	1.48
Nitrocellulose (NC)	1.51	Paraloid B-72 (ethyl methacrylate/ methylacrylate)	1.49
Window glass	1.52	Paraloid F-10 (butyl methacrylate, 40% solution in mineral and aromatic solvent, 9:1 ratio)	1.49
Polyamide (PA 6 and PA 6.6)	1.53	Methyl cellulose	1.50
High-density polyethylene (HDPE)	1.54	HXTAL-NYL-1 (epoxy resin EPO)	1.52
Polyvinyl chloride (unplasticised, PVC-U)	1.54	Aquazol	1.52
Polyester (PET)	1.55–1.64	Unsaturated polyester resin (UP)	1.54–1.72
Styrene-acrylonitrile resin (SAN)	1.57	Fynebond (epoxy resin EPO)	1.57
Polycarbonate (PC)	1.59		
Polystyrene (PS)	1.59		

6.3.2. Transparent polystyrene

Transparent polystyrene can be glued with several types of adhesive. The selection includes acrylates (Paraloid B-72, Paraloid B-67, Primal AC 35) and epoxies (HXTAL-NYL-1, Araldite 2020). The weakest connection of these products is made by Paraloid B-67. HXTAL-NYL-1 keeps its clear, transparent tone the best, while the others become yellowish. HXTAL-NYL-1 also gives the most imperceptible join. All of the above can later be removed.[216]

For Paraloid B-72, it is better to use it in an ethanol solution, not an acetone solution. As acetone evaporates very rapidly, the adhesive solution quickly solidifies. Rushing could complicate achieving the desired outcome. Acetone can also harm the surface of the polystyrene. If using Paraloids, remember that they contract quickly as the solution evaporates. This is particularly important when filling in cracks and nicks. Paraloids also have the tendency to form air bubbles as they dry, which may appear in the weak spots of the glue joint and be a visual nuisance.[217]

When freshly mixed, HXTAL-NYL-1 is very runny, which may make it somewhat hard to apply. Yet it is well suited for filling in micro-cracks and nicks. In the latter case, it may prove necessary to repeat the process several times, to increase the thickness of the layer. It is also good to fill cracks with epoxies because there is only minimal shrinkage upon curing.[218]

It should be noted that the surface tension of epoxy adhesives is higher than that of polystyrene. This means that epoxy adhesives do bond to the polystyrene, but only weakly. This property can be advantageous in terms of reversibility, but adhesive joints under significant stress are likely to fail. If an extremely strong connection is needed, the use of cyanoacrylates (superglues) can be considered, but remember that they are not reversible and may damage the plastic.[219] Be sure not to use superglues on extruded polystyrene, since instead of a true adhesive bond, it will attack the material, creating holes.

The abovementioned adhesives can also be considered as suitable for joining opaque polystyrene.

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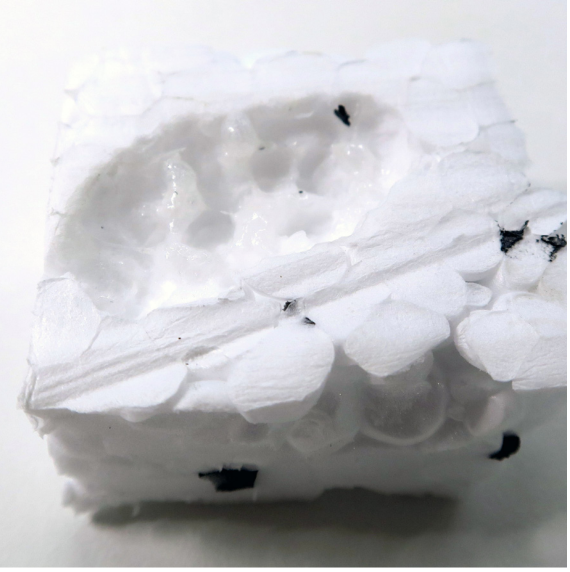
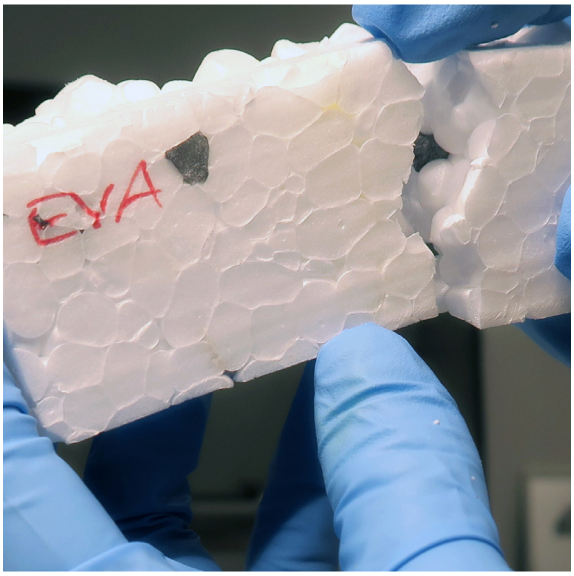
[216] Winther and others 2013.
[217] Winther and others 2013.
[218] Winther and others 2013.
[219] Winther and others 2013.

6.3.2.1. Polystyrene foam

Gluing extruded and expanded polystyrene foam is a bold undertaking, because the bulk of what we are gluing is air. Extruded polystyrene is more than 95% air. Be sure to make note of the solubility parameters when gluing plastic (the difference should be greater than 2). If the wrong product is selected, the glue will rapidly corrode a hole into the plastic.



Superglue works its way into expanded polystyrene in a few seconds, causing irreversible damage. Photograph by the author



Ethylene vinyl acetate performs very well as an adhesive for expanded polystyrene but its yellowish colour can stand out. The photo shows a test piece that broke when bent in a location other than the glue joint. To the left of the break, a yellowish trace of adhesive running diagonally can be seen. Photograph by the author

An aqueous dispersion based on thermoplastic acrylic polymer Plextol D 498 yields a good result, and is used mainly for gluing and consolidating ceramics, porcelain, wood, paper, leather, textile and plaster. When applied to surfaces, the adhesive sets reasonably quickly, allowing easy fixing of the areas that need to be repaired. A strong adhesive bond develops in just a few hours. After 24 hours, the joint is so strong that if you were to try and break the joined area, the material gives way in another place, not at the join. The glue is nicely transparent. Dispersion K360 and ethylene vinyl acetate (EVA) give almost as good a result. A drawback of these last two is the yellowish tone, and EVA is even more yellow than K360.

As acetone dissolves polystyrene foam, it should not be glued with Paraloid B-72 in an acetone solution. It is better to use Paraloid B-67 dissolved in white spirit. Yet another possibility is EVA hot glue. In this case, make sure the hot end of the glue gun does not touch the plastic and cause it to melt.

6.3.3. Polymethyl methacrylate

Consulting the refractive index table, we see that Acrifix 116 (n = 1.48) and Paraloids (n = 1.49) are suitable for gluing transparent acrylic (n = 1.49). Ethanol should be used as the solvent for Paraloid B-72, because acetone may dissolve the surface of acrylic plastics. An ethanol-based solution of Paraloid B-72 will also dry more slowly, giving more working time.

Acrylic can also be glued with epoxy resins. Although the refractive index of for HXTAL-NYL-1 varies by 0.03 from that of acrylic, it does result in a nearly imperceptible join. To make epoxy more viscous, it should be covered (but not airtight) and left to sit for a few hours before using it. HXTAL-NYL-1 cures slowly (a week or so).[220] Likewise, epoxy at the consistency of water is ideal for filling in scratches. Excess glue is allowed to harden into gel (24 hours) and then it can be removed mechanically.[221]

6.3.4. Gluing polyethylene and polypropylene

Polyolefins are intrinsically "waxy" plastics, meaning it is difficult to glue them. This is confirmed by the fact that the word "plastic*" appears on most superglue packaging, along with the names of other glueable materials. Under the asterisk we find a note stating that the glue does not adhere to polyethylene or polypropylene. But one superglue has proved its worth – Loctite Super Attak Plastic. It consists of an activator and an adhesive. The activator is the key, changing the polyethylene's surface properties to enable an adhesive bond. The glued surfaces adhere quickly and any glue that seeps out of the joint can later be easily removed, because it only adheres to the surface primed by the activator. The bond is medium strength, but it may break if bent or forced.

6.3.5. Gluing polyurethanes

Polyurethane plastics take many different forms. The object may be hard, soft, rigid or elastic. The material may also be foamed, and in this case, the products can also differ (rigid, semi-rigid or soft foam). Therefore, the right choice of glue depends on the properties of the polyurethane.

EPO glues, paraloids, and Bison Combi Plastic (a polyurethane-based adhesive) are suitable for rigid polyurethane (including foamed polyurethane).

Artificial leather made of polyurethane has been successfully glued and consolidated with acrylic glue dispersions Lascaux 498HV and 360HV[222], Paraloid B-72 (a 1% solution of 2 : 1 ethanol to acetone mixture), and an aqueous solution containing 20–24% Impranil DLV.[223]

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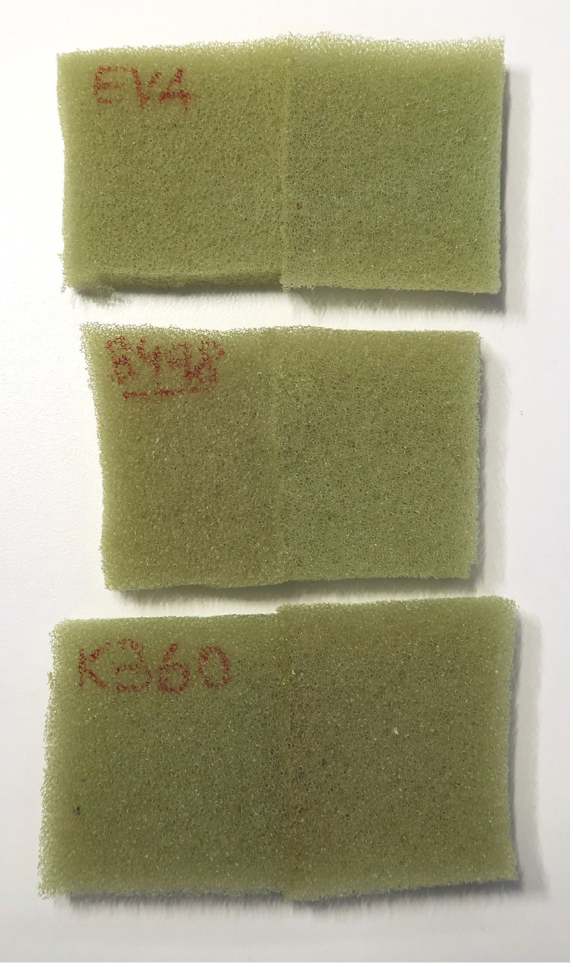
[220] O'Connor 2015.

[221] Lagana, van Oosten 2011.

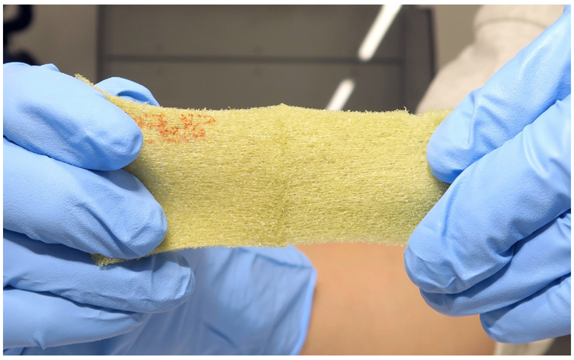
[222] Schertel 2006.

[223] Castaneda 2014.

Soft foam can be glued with Bison Soft Plastic (polyester urethane glue) available at retail, or with conservation-grade adhesives, Plextol B498 and ethylene vinyl acetate (EVA). The rapidly setting bonds remain elastic and transparent. The most elastic and least perceptible result comes from water-based Dispersion K 360.



Gluing of ether-based polyurethane foam. Plextol B498, EVA and dispersion K360 all performed very well. The best option was K360, as the adhesive bond stayed the most elastic. Photographs by the author



6.3.6. Gluing polyvinyl chloride

Rigid PVC can be glued with epoxy adhesives and paraloids. Bison Hard Plastic (a PVC-acrylate copolymer) also works extremely well.

Plasticised polyvinyl chloride, like natural rubber, is an elastic material. Therefore, the glue that is used must remain similarly elastic. The best option available at retail is Bison Vinyl Plastic. The surfaces coated with the adhesive adhere quickly and strongly. After 24 hours, the bond is even strong enough to be stretched. Plextol B 500 also produces a good result.

A superglue meant for PVC-P enabled repair of the damage caused by the rabbit. Photographs by the author

6.3.7. Gluing celluloid and cellulose acetate

If a durable adhesive bond is desired, pure acetone is the best. The solvent is applied to both surfaces and left to dissolve for a short time on each surface before being pressed together, which results in a strong bond. It must be remembered that the adhesive bond comes at the expense of the existing plastic, i.e. the form may change due to loss of material. It is therefore wise to mix a paste from acetone and spare plastic. When applying the paste, keep in mind that the acetone in the paste will dissolve the object's surface and as acetone evaporates from the paste, it will also shrink markedly.

If glues are to be used, epoxies, polyurethane glues and acrylic glues are suitable. Before applying the adhesive, the surface should be cleaned with isopropanol.

Shards of celluloid from a sharp blow administered with a hammer can be joined using acetone. The procedure is a bit more complicated if the item has been in a broken state for a few years – the fragments become deformed and no longer fit together precisely. Photographs by the author

Overview of the glues most commonly used for gluing and consolidating plastics

Plastic	Adhesive	Comments
Nitrocellulose Cellulose acetate	EPO glues polyurethane glues acrylic glues	Before gluing, clean the surfaces with isopropanol. Bear in mind that if the glue contains acetone, it will dissolve the plastic.
Casein formaldehyde Phenol formaldehyde Urea formaldehyde Melamine formaldehyde	EPO glues polyurethane glues acrylic glues	Before gluing, the surfaces should be cleaned with isopropanol.
Unsaturated polyester resin	EPO glues	Refractive indices need to be consulted.
Polyethylene Polypropylene	EPO glues Loctite Super Attak Plastic	Plastics with non-adherent surfaces. A better result is obtained by roughening the surface beforehand with fine sandpaper.
Polystyrene Polystyrene foam	acrylic glues EPO glues water-based glues	Polystyrene dissolves quickly in acetone.
Polyurethane Polyurethane foam	polyurethane glues EPO glues Bison Soft Plastic EVA Plextol D 498 Dispersion K 360	It needs to be confirmed in the case of polyurethane foam, that the glue bond will remain as elastic as the foam.
Polyamide (Nylon)	EPO glues	The adhesive bond will not be particularly durable.
Polycarbonate	EPO glues polyurethane glues cyanoacrylates acrylic glues	Refractive indices need to be consulted.
Polymethyl methacrylate	EPO glues polyurethane glues cyanoacrylates acrylic glues	Refractive indices need to be consulted.
Polyvinyl chloride Plasticised polyvinyl chloride	Plextol B 500 Bison Vinyl Plastic	The glue used for plasticised PVC must be elastic.

6.3.8. Glues suitable for joining plastics

6.3.8.1. Water-based glues

Aquazol

- Water soluble synthetic resin (granules).
- Thermoplastic polymer: poly(2-ethyl-2-oxazoline).
- Dissolves in most organic solvents (water, ethanol, isopropanol, acetone).
- There are four versions of Aquazol, which vary from each other in terms of molecular mass. Aquazol 500 (AQ500) has the highest molecular mass (the strongest), followed by Aquazol 200 (AQ200), then Aquazol 50 (AQ50) and Aquazol 5 (AQ5).
- Withstands weak acids and bases.
- Non-toxic.
- Mould-resistant.
- Appears blue under UV light.
- Glass transition temperature: 69–71 °C
- pH 6.8–7.4
- Refractive index: n = 1.52

Drawbacks:
- Hygroscopic! Becomes sticky in high RH, and therefore not suitable in environments with high relative humidity (RH > 65%).
- If exposed to high relative humidity, viscous flow may appear.
- Not advisable to use for gluing or consolidating load-bearing areas.
- Aquazol's solubility in water and other common solvents can become a problem if the consolidated or glued object is later cleaned.

Use:
- Aquazol has been used for gluing and consolidating glass, ceramics, paintings on canvas (oil, gouache, acrylic), paintings on glass, wood polychrome and watercolour paintings, clay figures and paper. It has also been used in preparations for gilding work or as fillings.

- **As a glue:**
    - Glues many polymers – as well as wax!
    - AQ500 is the best for gluing. Yet if greater penetration is required, surfaces should be primed with AQ200. When preparing a low-viscosity dilute solution of AQ500, its polymer chains are still too long to fit between the molecules of the material, so the glue bond may remain weak. The dilute solution also has insufficient "glue" for yielding a strong enough bond.
    - If two larger pieces have to be glued together, Aquazol-solvent gel can be used. The gel is very sticky and keeps the pieces from slipping. As it dries, the polymer pulls the pieces nicely together.
    - An aqueous or alcohol-based solution of Aquazol has been used for gluing ivory, bone, polyester resin and veneers.

- **As a consolidant:**
    - The best option would be AQ200. AQ500 does not penetrate enough into the cracks, and AQ50 does not have strong enough adhesion.
    - For the most part, polymer granules are dissolved in water, ethanol or isopropanol to make a 5–10% solution (5–10 g of adhesive per 100 ml of solution).
    - Low-viscosity solutions can be applied to the surface using a nebulizer, and more viscous ones with a syringe or a brush. A mister is good for finishing matte, powdery paint coats, using a 1.5% aqueous solution of AQ500, to which a little ethanol has been added (usually the finishing must be carried out several times to ensure total consolidation).
    - Aquazol stains and excess coats can be removed with deionised water. It is advisable to do this before the polymer has dried completely. Dry Aquazol can be successfully removed with acetone.
    - AQ50 can be used instead of isinglass. It has similar properties, but unlike isinglass it does not shrink when drying.
    - To achieve the best possible adhesion, mix AQ500 and AQ200 1:1, in a 1:1 solution of ethanol and water. This solution is used for consolidating gilded wood.

- **Retouching:**
    - Aquazol can be blended with pigments and used to retouch gouache, watercolour, acrylic or oil paintings. Lower molecular mass Aquazols mix with pigments better. AQ500 may leave a film on the surface and peel off.
    - The solutions must be as viscous as possible. 67% AQ50 solution, 33% AQ200 solution and 20% AQ500 solution. Solutions can be diluted as needed. (Used instead of gum arabic, as it is less hygroscopic.)
    - There is a risk that Aquazol will remain shiny in the retouched area and not completely harden.
    - There is also a risk that Aquazol may become a little yellowish over time, due to which it is only suitable for retouching darker tones.

- **Other uses:**
    - As a barrier layer when recording inventory numbers on amber. The barrier layer must be coated with a layer of Paraloid, because Aquazol is hygroscopic and already becomes sticky when breathed on. A ~10% aqueous solution of AQ200 is suitable as a barrier layer.

More reading:

- **Arslanoglu**, Julie; **Tallent,** Carolyn. Evaluation of the use of Aquazol as an adhesive in paintings conservation. – *WAAC Newsletter*, Vol. 25, No. 2, May 2003, http://cool.conservation-us.org/waac/wn/wn25/wn25-2/wn25-205.pdf
- **Arslanoglu,** Julie. Aquazol as used in conservation practice. – *WAAC Newsletter*, Vol. 26, No.1, January 2004, http://cool.conservation-us.org/waac/wn/wn26/wn26-1/wn26-105.pdf
- **Bosetty**, Elisabetta. A comparative study of the use of Aquazol in paintings conservation. – *e-conservation*, No. 24, Autumn 2012, https://issuu.com/elisabettabosetti/docs/a_comparative_study

Dispersion K 360

- An aqueous dispersion based on a thermoplastic acrylic polymer.
- 2-ethyl hexyl acrylate.
- A pressure-sensitive glue that adheres to many materials and retains its stability with temperature change.
- Water is the only solvent.
- Non-flammable.
- Concentration: ~60% (w/v)
- Glass transition temperature: −31 °C (elastic and sticky at room temperature)
- pH 2–2.5

Use:
- D K360 is meant for use as a self-adhesive layer for many materials, such as textile, film, paper, sheet metal, glass and expanded plastic.
- Adopted in late 2015 as a replacement for Plextol D 360. In general, they are glues with very similar properties, but their pH levels are quite different from one another (P D360 pH = 8).
- D K360 can be applied onto material using a brush, a mister or impregnation.
- D K360 can be mixed with other Plextol emulsions, and so change its properties.

EVA neutral glue

- Ethylene vinyl acetate (emulsion).
- In principle, the same as BEVA 371.
- Plasticiser-free (the ethylene molecules are already elastic by nature).
- Contains calcium carbonate, which serves as a glue stabiliser.
- More stable and a better option than PVA (polyvinyl acetate). Also has better adhesion powers. PVA contains plasticisers, which migrate to the material being glued and break down over time into acidic compounds. But this type of acidic hydrolysis does not take place with EVA.
- EVA is used in the form of glue sticks for a hot glue gun.
- Boiling point: ~100 °C
- pH 7–8

Drawbacks:
- Glossy.
- Potential mildew growth has been observed on EVA (and PVA). To hinder mildew, fungicides are added to the glue, but they wear off after a while. It is therefore advisable to use up the glue within 3 years of opening the bottle. The brush should never be dipped into the bottle a second time after application. Nor should glue that has already been poured out and used be returned to the bottle. The glue bottle cap must be properly closed while not in use.

Use:

- Water-soluble glue that is ideal for binding work and gluing paper and cardboard in general. Suitable for conserving leather and canvas paintings.
- Do not refrigerate!
- To prolong drying, EVA can be mixed with methylcellulose.
- To repair tears on paper, canvas and leather, EVA can be applied beforehand and allowed to dry on a patch (such as Reemay® – 100% polyester fabric) which is then applied over the tear and activated by using a hot spatula to heat it from the top.

More reading:

- Williams, Donald C. Some experiences with flexible gap-filling adhesives for the conservation of wood objects. – *Facing the Challenges of Panel Paintings Conservation: Trends, Treatments, and Training*. The Getty Conservation Institute, 2009, pp 113-124,

https://s3.amazonaws.com/theBarn/Articles/Conservation/Williams,Don-Gap_Filling_Adhesives.pdf

Lascaux Medium for Consolidation

- A low viscosity acrylic resin dispersion.
- Dissolves in esters, acetones, and aromatic solvents.
- Matte, elastic, light and ageing-proof, short drying time, very good adhesion powers.
- Boiling point: ~100 °C
- pH 8–9

Use:

- For consolidation: paintings (tempera, acrylic, oil), polychrome, paper, cardboard, textile, wood, concrete, plastic.
- Before using, surfaces can be dampened with white spirit. Excess adhesive can be removed with acetone after 24 hours.

Plextol B 500

- Copolymer of ethyl acrylate and methyl methacrylate (dispersion).
- Thermoplastic.
- Medium hardness, medium viscosity, withstands cold well.
- Withstands ageing well.
- Dissolves well in xylene, toluene and acetone.
- Milky liquid, concentration ~50%
- Boiling point: ~100 °C
- Glass transition temperature: ~9 °C
- pH: 9–10

Use:

- Consolidation material for paper, cardboard and plastic. The dried glue film can be activated by heating, for use in canvas restoration or repairing. Consolidation of ethnographic objects (fixing flaking paint).
- Has been used for conserving oil paintings for nearly 30 years.
- Especially good consolidation material for loose matte paint.
- Dissolved in toluene, Plextol B500 can be used as a glue. This kind of solution can also be applied to film, allowed to dry, and the dry glue sheet peeled off the film and later reactivated with a hot spatula on the desired surface for gluing.
- Diluted, it can be mixed with watercolours (colour pigments) and used for retouching.
- For consolidating gilding work.

More reading:

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Plextol D 498

- Dispersion of methyl methacrylate and butyl acrylate.
- Medium hardness (harder and more viscous than Plextol B 500), good friction resistance and water resistance.
- Concentration: ~50%
- Boiling point: ~100 °C
- Glass transition temperature: ~13 °C
- pH 9

Use:

- Used as a binder for weather-resistant paints. Suitable for gluing and consolidating ceramics, porcelain, wood, paper, leather, plastics, textile and plaster.
- Very good for gluing expanded and extruded polystyrene. Also for gluing and consolidating foamed polyurethane.

6.3.8.2. Other glues

Araldite Rapid

- Two-component epoxy resin.
- Does not shrink while curing.
- Use within 5 minutes of combining the components.
- Cure time: the surfaces being glued can be adjusted within 4 minutes, adhesion takes place within 30 minutes, complete drying takes 4 hours.
- Solvent-free. Resistant to oils and many chemicals.
- Colour tone: slightly yellow.
- Temperature range suitable for use: –30–65 °C
- Refractive index: $n = 1.47–1.48$

Use:
- Used for gluing glass, metal, wood, ceramics, plaster, concrete, leather, cardboard, textile, rubbers and plastics (other than polyethylene, polypropylene and Teflon).
- To achieve better adhesive bonding, the surfaces should first be roughened and cleaned with isopropyl alcohol or acetone.
- Components are mixed 1 : 1. Mix for 30 seconds. Avoid mixing it too vigorously (this will cause many air bubbles). Caps must be immediately screwed back onto the tubes of glue and hardener (Important: Make sure that the right cap goes back onto the right tube!).
- Glue is applied to both surfaces. The adhesive assembly must be securely fixed into place while the glue cures as it takes several hours. Extra glue that oozes out from the contact area can be mechanically removed after 10–20 minutes have passed, by which time the glue will have solidified into a gel.

More reading:
- Product sheet:

https://polyestershoppen.nl/download/araldite-rapid-epoxylijm/araldite-rapid-data-sheet-145.pdf

Araldite 2020

- A low viscosity two-component epoxy resin.
- Does not shrink while curing.
- Solvent-free. Resistant to oils and many chemicals.
- Transparent.
- Use within 40–50 minutes of combining the components.
- Cure time: 16 hours at room temperature, complete hardening 25 hours.
- Refractive index: $n = 1.553$

Use:

- Well suited to gluing glass and ceramics and for creating transparent cast forms and laminates. In addition, metal, wood, plaster, marble, concrete, leather, cardboard, textiles, rubbers and hard plastics can also be successfully glued (except for polyethylene, polypropylene and Teflon).
- The surfaces to be glued should first be cleaned using isopropanol or acetone.
- Components A and B must be mixed at parts per weight of 100 : 30 or parts per volume of 100 : 35.

More reading:

- Product sheet: https://samaro.fr/pdf/FT/Araldite_FT_2020_EN.pdf

HXTAL-NYL-1

- A low viscosity two-component epoxy resin.
- Does not shrink while curing.
- Transparent, does not yellow as it ages.
- Use within/cure time: 2/7 days
- Glass transition temperature: 47 °C
- Refractive index: n = 1.515

Use:

- Used for gluing glass and transparent plastics (polycarbonate, acrylic, and if a weaker bond is desired, polystyrene), marble, porcelain, stone, metal and wood or for filling in gaps. It can be readily tinted with pigments and compacted with fillers. May be used as a porcelain glaze.
- A brush or nebulizer can be used for application (diluted with toluene and xylene).
- The compound must be prepared of two components in a ratio of 3 : 1 (resin to catalyst). The mixed glue can be stored in a refrigerator for up to a week in an airtight container.
- At room temperature it will solidify completely in about 7 days (with a sufficiently strong bond within 24 hours). Any excess glue should be cleaned off after 24 hours when it can be cut with a scalpel.
- Freshly mixed glue is very liquid and may prove to be complicated to work with. To make the compound more viscous, it should be covered (but not airtight) and allowed to sit for a few hours. However, freshly prepared liquid glue is a good means of filling fine cracks and gaps through capillary action. So that the glue is able to seep more readily into the cracks, the item could be heated slightly (with a blow dryer on low heat). The glue should definitely not be heated (it will turn yellow).
- Since HXTAL takes a long time to dry and is quite liquid at first, the parts being glued must be securely clamped. Once the glue has cured for a few days, it is no longer possible to separate them.
- The surfaces to be glued should be cleaned beforehand using isopropanol.
- If there is a need to glue together, e.g., two blocks of glass, the weight of the top block

may be heavy enough to force too much glue out from the glued surface. The glued layer will therefore remain too thin for a strong connection. To avoid this, thin spacers can be positioned between the blocks, to leave a slight slit between them so that there would be room for the glue.

More reading:

- *Using Hxtal NYL-1 Clear Epoxy* – Instructions, http://www.lakesidepottery.com/HTML%20Text/Tips/Hxtal-NYL-instructions-glass-epoxy.htm
- **Tennet**, Norman H.; **Koob**, Stephen P. An assessment of polymers used in conservation treatments at the Corning Museum of Glass. – *Glass and Ceramics Conservation* 2010, Interim Meeting of ICOM-CC Working Group, 2010, http://www.icom-cc.org/54/document/wg-glass-and-ceramics-interim-meeting-corning-2010--preprint-tennent/?action=Site_Downloads_Downloadfile&id=1282
- **Koob**, Stephen P. Tips and tricks with epoxy and other casting and molding materials.– *AIC Objects Speciality Group Postprints*, Vol. 10, 2003, http://resources.conservation-us.org/osg-postprints/wp-content/uploads/sites/8/2015/02/osg010-14.pdf

Paraloid B-72

- Thermoplastic acrylic resin (ethyl methacrylate/methyl methacrylate, 70/30).
- Granules.
- Dissolves in aromatic solvents (toluene, xylene, acetone), ethanol, isopropanol. Depending on how rapidly the solvent evaporates and its quantity, the polymer cure time can be controlled.
- Does not dissolve in white spirit, water, oils, fats.
- Light-resistant and withstands ageing well.
- Medium hardness. Stronger than PVA but more elastic (and also more elastic than Paraloid B-67).
- Glass transition temperature: Tg = ~40 °C
- Melting point: ~150 °C
- Refractive index: n = 1.479–1.489

Drawbacks:

- Can only be removed by dissolving in acetone, but can also damage the plastic. Therefore it is not advisable to use on any plastics that dissolve in acetone.
- Becomes yellowish over a longer period of time.

Use:

- One of the more stable polymers used in conservation. Adopted as a replacement for PVA.
- Consolidation (mural paintings, plaster, wood, ceramics, bone, glass, etc.), fixative (charcoal, chalk and pastel drawings), gluing (glass, ceramics, bone, wood, etc.), varnishing paintings.
- Used as a barrier layer between object and marker when recording inventory number on an item and as a varnish layer applied over the marking (in this manner, the marking is later completely removable). For this a 25% solution of B-72 in acetone can be used (Note: not suitable for all materials).
- Suitable for retouching finishes on wood surfaces. Especially good if the surface was previously covered with materials sensitive to water or other polar solvents (such as alcohols). A solution of Paraloid B-72 in an aromatic hydrocarbon allows surfaces to be retouched without impacting the original finish. At the same time, the surface worked on with B-72 can later be finished using a traditional method (e.g. waxing, oiling, gilding).
- 10–20% solution in acetone, toluene or xylene is used as a varnish. The speed of drying can be reduced by adding ethanol to the solution. After dissolving these solutions, up to 40% ethanol can be added. A solution mixed with ethanol may be a milky colour but nicely transparent when dry. The varnish withstands light well and does not react with colour pigments.
- 2–5% solution is used as a fixative for crumbly matte paints (risk of leaving a “halo”).
- Used as a structural reinforcer for wood that has become crumbly.
- Paraloid B-72 can be used to cast suitably sized acrylic plastic chips for filling holes in ceramics, glass or transparent plastic. It has to be taken into consideration that B-72 shrinks quite significantly as it dries.
- It is possible to use it as a barrier for epoxy resins on the surfaces being glued (such as bone).

More reading:

- **Mortise and Tenon Magazine blog**, How to mix a weight/volume Paraloid B-72 solution, 04.12.12,

http://www.workbenchdiary.com/2012/12/how-to-mix-weight-volume-paraloid-b-72.html

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http://cool.conservation-us.org/jaic/articles/jaic40-01-002.html, retrieved 19.09.17.

Paraloid B-67

- Polybutyl methacrylate
- Transparent granules.
- Dissolves in hydrocarbons (toluene, xylene, benzene, acetone, petrol, white spirit, turpentine) and isopropanol (forms a gel).
- Leaves a rather glossy surface, but becomes matte over time.
- Waterproof.
- Can be polished.
- Refractive index: n = 1.486
- Glass transition temperature: Tg = 50 °C

Drawbacks:

- As the glass transition temperature of B-67 is quite low, it remains relatively elastic at room temperature, even sticky, binding dust and dirt.
- As it ages, it becomes fragile. In the presence of light and oxygen, the polymer chains become cross-linked, making B-67 increasingly less soluble. This reduces the reversibility of the work done.
- If B-67 is used as a varnish layer, it may become brittle and dull in a few decades, and peel off the surface.
- Becomes yellowish over time.
- If the polymer was dissolved in benzene or turpentine, it will dissolve oil paints and waxes.
- Less stable than Paraloid B-72.

Use:

- If a varnish needs to be prepared for application by brush, a good solution is 8–10% or for more viscosity, 15–20% using white spirit, xylene or a blend of the two. A 30% solution is suitable for using as a top coat. A 10–15% solution is appropriate for misting.
- A coat of varnish applied by brush will remain sticky for at least 5–10 minutes. Drying may take several hours.
- Mixed with pigments, can be used for retouching (dissolved in turpentine, for example).

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http://www.conservation-wiki.com/wiki/V._Polymeric_Varnishes

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APPENDICES

Appendix 1. Abbreviations of the names of selected polymers

Abbreviation	Full name	Commonly referred to as
ABS	Acrylonitrile-butadiene-styrene polymer	ABS
CA	Cellulose acetate	Acetate
CN / NC	Cellulose nitrate, nitrocellulose	Celluloid
CS	Casein formaldehyde (Casein)	Casein, Galalith
EP (EPO)	Epoxy resin	Epoxy
HDPE	High-density polyethylene	Polyethylene
HIPS	High-impact polystyrene	-
LDPE	Low-density polyethylene	Polyethylene
MF	Melamine formaldehyde	Melamine
NR	Natural rubber (cis-1,4-polyisoprene)	Rubber
PA	Polyamide	Nylon
PC	Polycarbonate	Polycarbonate
PET	Polyethylene terephthalate	Polyester
PE	Polyethylene	Polyethylene, polythene
PF	Phenol formaldehyde	Phenolic, Bakelite
PLA	Polylactic acid	Polylactide
PMMA	Polymethyl methacrylate	Acrylic, Plexiglas
PP	Polypropylene	Polypropylene
PS	Polystyrene	Polystyrene, Styrene
PUR	Polyurethane	Foam rubber (expanded plastic)
PVAc	Polyvinyl acetate	PVA
PVAl	Polyvinyl alcohol	-
PVC	Polyvinyl chloride	Vinyl
UF	Urea formaldehyde	Aminoplast (Urea)
UP	Unsaturated polyester	-
UPVC, PVC-U	Unplasticised PVC	Plastisol
EPS	Expanded polystyrene	Expanded polystyrene
XPS	Extruded polystyrene	Styrofoam

Source: Christjanson 2003: 113–115

Appendix 2. Use of plastics and several key events

Year	Event
1521	**Natural rubber** – In a travel diary, Spaniard Pedro Mártir de Anghiera describes seeing indigenous Haitians playing with rubber balls. A select number of Europeans learn of an amazing elastic material.
1751	**Natural rubber** – The French Academy of Sciences releases research by François Fresneau and Charles Marie de La Condamine on rubber trees and use of rubber. Rubber imports begin and inventors are offered this new material for demonstrating their ideas. Among other items, suspenders for socks begin to be produced.
1823	**Natural rubber** – The Scotsman Charles Macintosh laminates a layer of rubber between two sheets of fabric, thereby producing a waterproof material. Waterproof raincoats go on sale.
1851	**Ebonite** – Thomas Hancock and Charles Goodyear introduce items made of ebonite (natural rubber) at the London World's Fair.
1862	**Nitrocellulose** – English metal specialist Alexander Parkes introduces objects made of parkesine (nitrocellulose) in London. Production of parkesine items starts in England.
1868	**Nitrocellulose** – the Hyatt brothers invent billiard balls made of artificial ivory.
1872	**Celluloid** – The Hyatt brothers' artificial material is patented as celluloid. The age of semi-synthetic materials begins.
1889	**Chardonnet silk** – French inventor Count Hilaire de Chardonnet starts making a highly flammable artificial silk from nitrocellulose fibres. Kodak **celluloid photographic film** goes on sale in America.
1895	The Lumière brothers produce the first celluloid cine-film in the world, depicting a train pulling into a station.
1897	**Casein formaldehyde** or galalith.
1898	Shellac is used to mass-produce gramophone records that remain popular until vinyl appears in the 1940s.
1900	University of Tartu pharmacy professor Ivan Kondakov publishes a method for the synthesis of **dimethylbutadiene**, initiating the production of synthetic rubbers.
1903	Kodak starts production of **cellulose acetate safety films**.
1908	**Bakelite** – Leo H. Baekeland introduces phenol formaldehyde to the world, which he names Bakelite. The age of synthetic polymers begins.
1909	**Bakelite** – Consumer goods begin to be made of Bakelite.
1920s	**Viscose** (Rayon) begins to be produced – a fabric made of semi-synthetic fibres derived from cellulose.
1926	Harrods, the most prestigious department store in London, puts **urea formaldehyde** products on sale (Beetle).
1927	**Catalin** – The American Catalin Corporation starts producing radio coverings made of transparent phenol formaldehyde without fillers. **Cellulose acetate** – The production of cellulose acetate sheets and rods for commercial purposes begins. **Urea formaldehyde** consumer goods. **Polystyrene** consumer goods.
1930s	A transparent adhesive tape (cellulose acetate, Scotch Tape) is invented.

1934	Elsa Schiaparelli uses **zippers** made of nitrocellulose and cellulose acetate in her fashion creations.
1935	**PVC** – The first PVC pipe is installed in Germany.
1936	**Acrylic** – Acrylic production begins in the UK.
1937	DuPont chemists discover **Teflon** (polytetrafluoroethylene).
1938	**Polyamide** – A toothbrush with plastic bristles (Dr. West's Miracle-Tuft Toothbrush).
1939	**Polyamide** – 64 million pairs of nylon stockings were sold. **Melamine formaldehyde** consumer goods.
1940s	**Polyethylene** – the English insulate aircraft radars with polyethylene.
1940	In Argentina, ballpoint pens invented by László Bíró start to be made of **polystyrene**.
1942	The first acrylic paint (PMMA, dissolved in turpentine). Earl Tupper patents polyethylene food storage containers (Tupperware).
1947	**Polyurethane**, USA.
1948	**HIPS** (high-impact polystyrene).
1949	**PVC-P** – Vinyl artificial leather. Foam rubber padding.
1950s	Nitrofilm production is discontinued.
1950	**Polyester film** – Polyester film starts to be produced in the USA under the brand name Mylar.
1951	Production of polystyrene foams (**EPS and XPS**).
1954	**HDPE** production in Great Britain. **Polypropylene** is discovered by Giulio Natta.
1955	Lego produces new toy bricks from cellulose acetate. American Express issues the first plastic credit card in the USA. (PVC) Lycra (polyurethane fabric) **Polycarbonate** appears at retail.
1959	Barbie doll (PVC-P).
1959	Plastic shopping bags (Sweden, Celloplast). **Polypropylene**.
1960s	**PVC-P** – Mary Quant's raincoat collection "The Wet Collection". PVC-P finds itself a role in the fashion industry.
1977	Motorola introduces the first mobile phone.
1979	The first artificial human heart is surgically inserted (mainly polyurethane).
1982	Steve Jobs assembles his first Macintosh in his home garage. **Polycarbonate** – compact disc (CD) is introduced.
1984	Plastic recycling system symbols are developed.
1988	The first car with polycarbonate headlight glass (Opel Omega) goes on sale on the European market.

* The information in the table is from sources listed in the bibliography and the additional reading list.

Appendix 3. Use of plastics in Estonia

Year	Development
1922	Albert Laretei with two assistants makes combs from bovine horn in a small shed in Tartu. (Beginning of the Estonian Comb Factory.)
1920s	Production of celluloid combs. Albert Laretei makes combs from galalith – artificial horn.
1934	The company Arba (from armatuur (fixtures and fittings) + Bakelite). It produces switches, wall sockets, plugs and other items for the Punane RET electronics plant and the Põhjala factory, and repair parts for cars and tractors.
1941	Industrial cartel Presto produces Bakelite buttons, haberdashery and toys.
1952	The first thermoplastic is introduced – plasticised PVC. Initially used for cable insulation and later artificial leather (Flora) and film (Artificial Horn factories). The Comb Factory launches production of celluloid table tennis balls.
1959	Local polyethylene processing begins. Primarily for cable insulation.
Late 1950s	Polystyrene enters production. It is adopted at Tartu Comb Factory in 1961, and at Artificial Horn factories in 1963. Gradually production of acrylic sheet begins.
1961	A blowing machine for plastic bottles is manufactured at Orto.
1962	The Central Committee of the Communist Party of the Soviet Union decides to reduce use of raw food materials in the technical field. This leads to a regulation that calls for the end of galalith production in artificial horn factories. The ENSV (Estonian Soviet Socialist Republic) Artificial Horn factories are the first to get extrusion machines for making polystyrene buttons.
1963	Buttons begin to be produced from polystyrene. Orto purchases a vacuum-forming machine that produces store signage from polystyrene sheets.
1964	Testing of polypropylene manufacturing begins. It takes a good amount of time to implement production of objects made from PP. Attempts are made to use the new material to make products that were otherwise made of polyethylene. Motorcycle helmet laws are introduced in the Soviet Union. Salvo starts testing helmet manufacturing. The helmets are made of high-impact polystyrene (HIPS).
Late 1960s	Production of expanded plastics. The main expanded plastics are polyurethane foam and polystyrene foam. Attempts are also made to introduce fibreglass reinforced resins. Examples are EPO and polyester resin reinforced with fibreglass or textiles. Chair components made of fibreglass start to be made at Orto.
1969	Tartu Comb Factory starts manufacturing polyethylene films.
1979	TPK (Tartu Plastic Products Testing Plant), starts producing combs from pelletised polypropylene.
1981	TPK discontinues celluloid comb production.

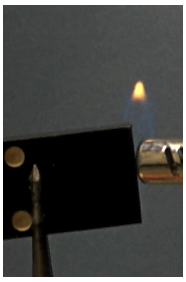
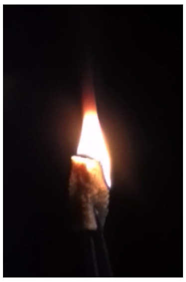
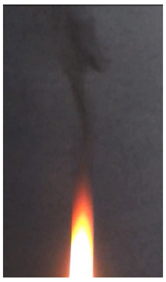
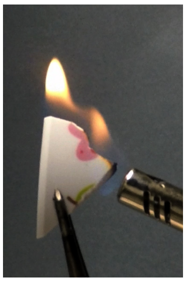
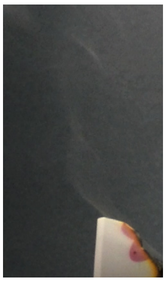
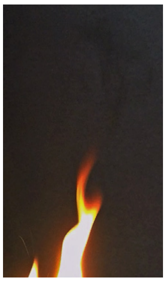
* The information in the table is from sources listed in the bibliography and the additional reading list.

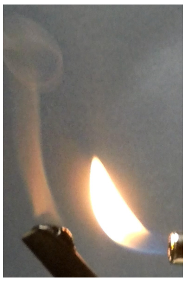
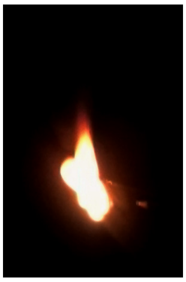
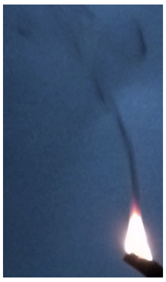
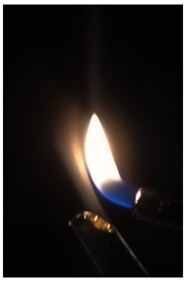
Appendix 4. Logos for the best-known local plastic producers during the soviet era

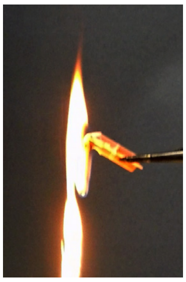
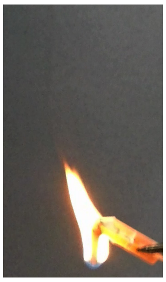
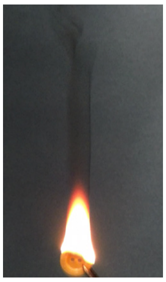
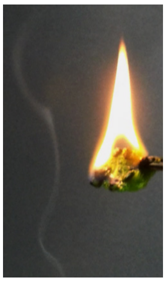
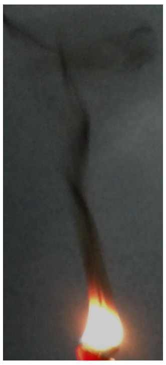
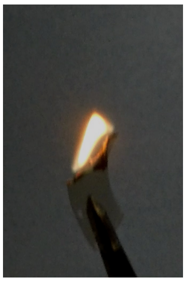
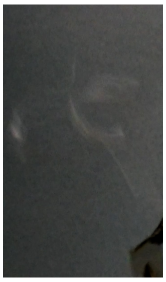
Logo	Comments	Material l	Main product
	Estoplast – 1959–2003. (Elektrometall + Presto) a new logo was designed in the mid-1960s, which was red and incorporated the company name.	PF PE (from 1961) PS PMMA	Lighting, installation equipment.
	Norma – from 1946, plastics production from the late 1950s.	PS PE	Toys (cars, boats), seat belts.
	Orto – from 1932, plastics production starting from 1965.	Fibreglass PE	Consumer chemicals, household cleaning products, plastic packaging, chairs components, marine buoys.
	Salvo – 1948–1993. Plastics production starts in 1949.	PF MF PE PS PC	Helmets, sleds, skis and ski boots, stoppers, bowls, toys, buckles, chess pieces, hair curlers, photo negative boxes.
	Tartu Kammivabrik – 1918. From 1930– Eesti Kammivabrik. From 1972 – Tartu Plastmasstoodete Katsetehas, From 1991 – AS Estiko Plastar.	Horn Galalith CN Vulcanite PE (from 1969) PS (from the 1970s) PP (from the 1970s)	Combs, pens, toothbrushes, eyewear frames, cigarette holders, hair ties, table tennis balls, rattles, swings, helmets, plastic bags and packaging.
	Punane RET – 1937, originally called OÜ Raadio-elektrotehnika tehas (RET).	PF PS (imitation ivory)	Radio-, sound reproduction-, cinema- and telescopic equipment and electronics, motorcycles and bicycles, photographic equipment.

Sources: Kruut 2011; Lageda, Kanne 1968; Kübar, H; Sepp, G. 1987; Punane RET – history.

Appendix 5. Identifying plastics with the burn test

Plastic	Combustion speed and description of flame	Photograph	Smoke description	Photograph	Emergent odour
Phenol formaldehyde (thermoset)	Does not ignite. Does not burn; material chars.		-	-	Distinct phenol odour; reminiscent of formalin.
Casein formaldehyde (thermoset)	Does not ignite. Does not burn; and if it should catch alight, the flame is weak and extinguishes quickly; material chars.		-	-	Smell of burning animal hair; scorched milk.
Natural rubber (thermoset)	Ignites quickly. The material is highly flammable; burns with an aggressive yellow flame.		Thick black sooty smoke.		Smell of burning rubber.
Melamine formaldehyde (thermoset)	Does not ignite. Does not burn; material chars.		Thin white smoke from the charred area.		No specific odour given off; what can be sensed is pleasant.
Nitrocellulose (thermoplastic)	Ignites very rapidly. Very aggressive, flickering yellow flame; gives off sparks and drips.		Thick black sooty smoke.		Burning conifer smell; reminiscent of pine resin.

Plastic	Combustion speed and description of flame	Photograph	Smoke description	Photograph	Emergent odour
Polyamide (thermoplastic)	Does not ignite. No flame; material melts.		Thin white smoke.	-	No specific odour given off; reminiscent of scorching.
Polyethylene (thermoplastic)	Ignites quite rapidly. Burns with a calm blue flame; melts and drips.		Thick white smoke.		Pleasant candle wax smell.
Polyethylene terephthalate (thermoplastic)	Ignites well. Very aggressive, uneven yellow flame; drips; crackles.		Thick black sooty smoke.		No specific distinguishing odour given off.
Polycarbonate (thermoplastic)	Does not ignite. Does not burn; melts.		Light transparent white smoke.	-	Reminiscent of gouache paints.
Polymethyl methacrylate (thermoplastic)	Ignites quite slowly. Calm, even, wide yellow flame with blue base; burning material melts and bubbles; does not drip.		Produces very little smoke.	-	Pungent, specific burning acrylic odour; easy to remember.

Plastic	Combustion speed and description of flame	Photograph	Smoke description	Photograph	Emergent odour
Polypropylene (thermoplastic)	Ignites quite rapidly. Calm at first, then broader aggressive yellow flame; drips.		Thick white and also black sooty smoke during combustion.		Mildly like candle wax; less perceptible than polyethylene combustion.
Polystyrene (thermoplastic)	Ignites quickly. Aggressive, broad yellow flame.		Thick black smoke; charred material fibre in the air along with the smoke.		Pungent odour characteristic of burning polystyrene; easy to remember.
Polyurethane (thermoplastic)	Ignites quite rapidly. Burns with a broad, calm yellow flame; melts and drips.		Calm, white smoke.		No specific distinguishing odour given off.
Polyvinyl chloride (thermoplastic)	Ignites quite rapidly. Calm flame; flame is greenish at the contact point of material, otherwise yellow; flame extinguishes after brief burning.		Thick black smoke.		No specific distinguishing odour given off.
Cellulose acetate (thermoplastic)	Ignites gradually. Calm, small yellow flame, which gains power but extinguishes after some time.		Dark, sooty flame while burning; thin and white as it extinguishes.		No specific distinguishing odour given off.

Appendix 6. Most common types of plastic degradation

Mechanical damage

- **Soiling** → The surface of the object is covered by everyday dirt, mud, dust, soot, but also, e.g. paint stains.

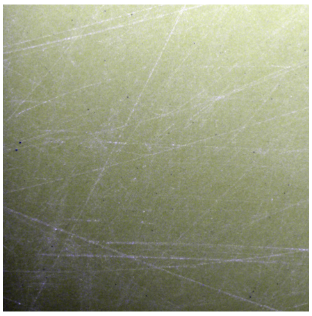
  Which plastics?
  - all plastics
  - soft, rough or bumpy surfaces, "greasy" plastics

  Risks:
  The soiled surface locks in moisture and contaminants. In addition, this keeps the VOCs from being released from some plastics, which is a part of their ageing. But if the acidic compounds are retained, the surface of the object becomes acidic. If high amounts of plasticisers have been added to plastic (e.g. PVC-P), which migrate over time to the surface, they "absorb" the dirt on the surface. It is later difficult or even impossible to remove. Therefore soiled surfaces must be cleaned if possible.

- **Scratches, friction** → Groups of little scratches on the item's surface or material wear.

  Which plastics?
  - all plastics

  Risks:
  Scratches allow moisture, oxygen and contaminants to penetrate the material, leading to further degradation processes. The scratches make the surface matte and can spoil the object's aesthetics.



- **Cracking, splitting** → Superficial or deeper damage. Splitting of the plastic's junctions and cracks caused by residual stress.

Which plastics?
- ◦ all plastics

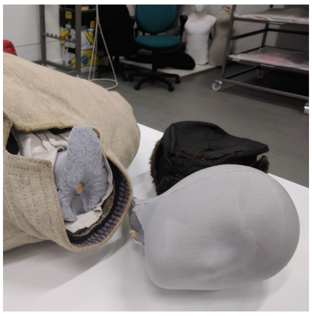
Risks:
It needs to be investigated whether the damage is mechanical or physical/chemical. If the object is brittle, dry, has shrunk and has many cracks, it may be a case of chemical damage. If the crack is either by itself or in a small cluster, it is probably mechanical damage. Just as with scratches, a number of harmful agents enter through the cracks. It is important to prevent chemical/physical ageing, as the damage might "grow" in depth and length.

- **Dents, deformations, holes, missing parts** → Deformation of the shape of the item or lack of integrity due to mechanical damage or unsuitable storage conditions.

Which plastics?
Dents, deformation:
- ◦ soft and elastic plastics (polyurethane foams, rubbers, PVC-P)
- ◦ thermoplastics (NC, CA, PE, PP, PS)

Holes, missing parts:
- ◦ all plastics

Risks:
The holes weaken the material and the damaging agents penetrate into the cavities. Over time, the shrinking material 'pulls' the cracks and fissures longer.

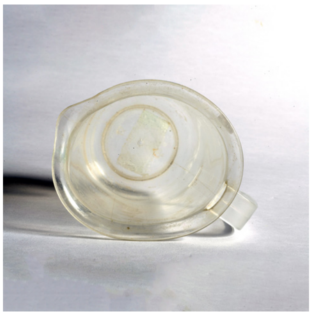


Physical and chemical degradation

- **Thermal damage** → Structural changes in polymer chains caused by sudden temperature fluctuations (hot, cold) or direct contact with a body of heat. Or by freezing.

  Which plastics?
  - mainly thermoplastics
  - all plastics

  Risks:
  Too high a temperature can cause irreversible deformation of the object. A longer period in higher temperature environments can markedly speed up the ageing process. If the object consists of several materials, a fall in temperature can cause tensions to arise in the junctions due to shrinkage, and lead to breakage.



- **Light damage** → Changes in the chemical makeup of the polymer due to UV radiation or damage to pigments. The light damage is visible as the object becomes yellowish or the pigments fade.

  Which plastics?
  - all plastics
  - light coloured plastics
  - PVC-P, PUR ether, natural rubber

  Risks:
  Depending on the type of plastic, light damage may be an aesthetic problem (e.g., PE, PS) or serious damage affecting mechanical, chemical and physical properties (e.g. PVC-P, PUR ether, vulcanised rubber). Plastic becomes brittle as a result of scission of polymer chains.

- **Oxidation →** Damage caused by oxygen and/or ozone, resulting in deterioration of mechanical and physical properties and appearance. Cross-linking or scission of the molecular chains occurs. The plastic becomes brittle and hard. Tensile strength and flexibility decrease and fragmentation results, colour changes gradually from yellowish to brown. The oxidation reaction gets its energy from UV light or heat.

  Which plastics?
  - all plastics
  - elastic and soft plastics (PVC-P, PUR ether, natural rubber)

  Risks:
  Oxidation is one of the most treacherous age-related degradation processes. Degradation occurs at the molecular level and the damaged material cannot be restored. To slow oxidation, objects should be kept in cool, dark, stable conditions.

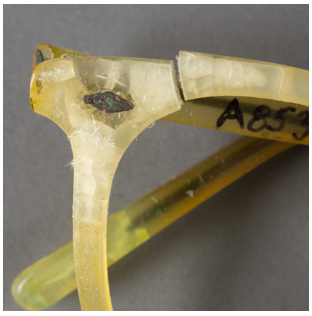
- **Hydrolysis** → Scission of the polymer's molecular bonds due to moisture in the air in an acidic/basic environment. The outcome of hydrolysis is deterioration of mechanical properties, decreased elasticity and weakening of the structure. The object's surface becomes acidic.

  Which plastics?
  - cellulose esters, polyesters, polyurethanes, expanded plastics, galalith, natural rubber

  Risks:
  Hydrolysis is the second-most significant ageing process after oxidation. Primarily because plastic is considered a waterproof material. Damage can be caused by damp-wiping, either the surface of the object itself or the shelf. It is essential to know that some plastics become extremely acidic over time and the acidic substances they give off may damage nearby objects.

- **Plasticiser and additive migration**

Note: The following plastics give off acidic gases or other harmful compounds:
- nitrocellulose (celluloid) – nitric acid
- cellulose acetate – acetic acid
- PVC-P – HCl, plasticisers
- vulcanised rubber – sulphuric acid, antioxidants
- PUR foam– nitrogen compounds



- **“Sweating”** → The surface of the object becomes sticky and glistens, as the plasticisers or anti-oxidants (vulcanite) are migrating onto it.

  Which plastics?
  - PVC-P, CA, vulcanite

  Risks:
  Phthalates migrate to the surface of PVC-P. The surface of the object is sticky, so it binds dirt to itself or sticks to other materials or objects. This is a serious case of degradation and signals that the storage conditions should definitely be modified. HCl catalyzes the ageing processes.

- **“Chalking”, “blooming“** → Parts of the object’s surface are covered by a powdery layer/crystalline material. These are additives or plasticisers (camphor) migrating from the polymer.

  Which plastics?
  - PVC-P, CA, NC

  Risks:
  If it is on the surface of PVC-P, the damage is harmless. But if crystals can be seen on celluloid, these may be nitrate salts. In this case, the material has become more brittle.

Biological degradation

- **Microorganisms and insects** → Damage caused by micro organisms and insect activity.

  Which plastics?
  - semi-synthetic plastics (NC, CA, galalith)
  - plastics that contain plasticising oils (PVC-P)
  - all plastics if there is suitable edible dirt on the surface

  Risks:
  Microorganisms ruin the appearance of the object and damage the surface layers with their activity. The storage room must not be too damp (RH > 65%). Insect excreta may cause chemical damage to the surface of the material. “Insect dirt” also binds moisture and creates favourable conditions for hydrolysis.

- **Signs of chewing** → Usually caused by rodents.

  Which plastics?
  - usually softer plastics

  Risks:
  Irreversible damage that may spoil the general appearance of the object and its mechanical durability.

Appendix 7. Reactions of consumer plastics with some solvents, acids and oils

Chemical	**LDPE**		**HDPE**		**PP**		**PVC**		**PC**		**PS**		**SAN**		**ABS**		**PMMA**		**PTFE**	
Temperature °C	20	50	20	50	20	50	20	50	20	50	20	50	20	50	20	50	20	50	20	50
Acetone	🟡	🟠	🟡	🟡	🟢	🟢	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🟡	🟠	🔴	🔴	🟢	🟢
Benzene	🟠	🔴	🟡	🟡	🟡	🟠	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🟢	🟢
Petrol	🟠	🔴	🟡	🟡	🟡	🟠	🟡	🟠	🟡	🟠	🔴	🔴	🟡	🟠	🟡	🟠	🟡	🟠	🟢	🟢
Potassium hydroxide (50%)	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🔴	🔴	🟢	🟡	🟢	🟡	🟢	🟡	🟡	🔴	🟢	🟢
Chloroform	🔴	🔴	🟠	🟠	🟠	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🟢	🟢
Xylene	🟠	🔴	🟠	🟠	🟠	🟠	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🟢	🟢
Nitric acid (10%)	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🟡	🟢	🟡	🟠	🟠	N/A		🟢	🟡	🟡	🔴	🟢	🟢
Nitric acid (70%)	🔴	🔴	🟠	🔴	🟠	🔴	🔴	🔴	🟠	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🟢	🟢
Methyl alcohol	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🟡	🟡	🟠	🟡	🟠	🟠	🟠	🟠	🔴	🔴	🔴	🟢	🟢
Sodium hydroxide (50%)	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🔴	🔴	🟡	🟡	🟢	🟢	🟢	🟢	🔴	🔴	🟢	🟢
Citric acid	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🟡	🟡	🟡	🟡	🟢	🟢	🟢	🟢	🟢	🟢	🟢	🟢
Formic acid	🟢	🟢	🟢	🟢	🟢	🟡	🟡	🟠	🔴	🔴	🟠	🔴	🟠	🔴	🟡	🟠	🔴	🔴	🟢	🟢
Vegetable oil	🟡	🟠	🟡	🟠	🟢	🟢	🟢	🟢	🟡	🟡	🟡	🟡	🟡	🔴	🟡	🔴	🟡	🔴	🟢	🟢
Turpentine	🟠	🔴	🟠	🟠	🟠	🟠	🟡	🟠	🟠	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🔴	🟢	🟢
Toluene	🟠	🔴	🔴	🔴	🟠	🟠	🔴	🔴	🟡	🟠	🔴	🔴	🟡	🔴	🔴	🔴	🔴	🔴	🟢	🟢
Hydrogen peroxide (30%)	🟢	🟠	🟢	🟢	🟢	🟠	🟢	🟢	🟢	🟢	🔴	🔴	N/A		🟠	🔴	🟢	🟢	🟢	🟢
Acetic acid	🟡	🟢	🟢	🟢	🟢	🟡	🟢	🟡	🟡	🟠	🟠	🔴	🟠	🔴	🟠	🔴	🔴	🔴	🟢	🟢

- 🟢 excellent resistance
- 🟡 good resistance (minor damage to surface of plastic)
- 🟠 poor resistance (solvent damages plastic's surface)
- 🔴 extensive surface damage or total dissolution

Sources: https://www.dynalon.com/CommerceManager/images/assets/Document/ChemicalPropertiesG-Z.pdf and https://www.dynalon.com/CommerceManager/images/assets/Document/ChemicalPropertiesA-F.pdf.

Appendix 8. Hildebrand solubility parameters for organic liquids and polymers

Solvent	Parameter (MPa1/2)	Polymer	Parameter (MPa1/2)
Diethyl ether	15.4	Polytetrafluoroethylene (PTFE)	12.6
White spirit	16.1	Polyethylene (PE) (while heating)	16.3
Turpentine	16.5	Polypropylene (PP) (while heating)	16.3
Xylene	18.0	Polybutadiene (PBD)	17.1
Toluene	18.2	Polystyrene (PS)	18.7
Ethyl acetate	18.6	Polymethyl methacrylate (PMMA)	18.2
Benzene	18.7	Polyvinyl chloride	19.4
Chloroform	19.0	Cellulose nitrate	21.6
Trichloroethylene	19.2	Polyethylene terephthalate (PET)	21.8
Acetone	20.4	Cellulose acetate	23.3
Butanol	23.2	Nylon 66 (PA)	27.8
Isopropanol	24.9		
Ethanol	26.0		
n-butyl alcohol	28.7		
Methyl alcohol	29.7		
Glycerine	33.6		
Water	47.7		

Source: Burke 1984.

Appendix 9. Glass transition temperatures and melting points for common plastics

Polymer	Tg ˚C	Tm ˚C
Natural rubber (cis-1,4-polyisoprene)	–70 (–58)	–
Nitrocellulose	53–56	80
Polyamide (nylon)	43–53	220–255
Polyethylene	−65–125	110–137
Polyethylene terephthalate	80	254
Polycarbonate	145–150	230
Polymethyl methacrylate	90–105	200–290
Polypropylene	–20–0	176
Polystyrene	100	240–290
Polyvinyl chloride (rigid)	81	175
Cellulose acetate	70–180	210

Sources: Christjanson 2008; Birley, Heath, Scott 1988; Brydson 1999; Horie 2006; Mauring 1985; Piiroja 1975; Rosen 1993; Shashoua 2008; Rubin 1990, Ellis, Smith 2008.

Appendix 10. Refractive index values for the most common transparent plastics and glues

Polymer	Refractive index (n)	Glue	Refractive index (n)
Cellulose acetate (CA)	1.48	so-called superglue (cyanoacrylate)	1.45–1.48
Polymethyl methacrylate (PMMA)	1.49	Polyvinyl acetate (PVA)	1.47
Polypropylene (PP)	1.49	Polyethylene vinyl acetate (EVA)	1.47–1.48
Low-density polyethylene (LDPE)	1.51	Acrifix 116 (polymethyl methacrylate PMMA)	1.48
Nitrocellulose (CN)	1.51	Paraloid B-67 (isobutyl methacrylate, 40% solution in mineral solvent)	1.48
Window glass	1.52	Paraloid B-72 (ethyl methacrylate/ methylacrylate)	1.49
Polyamide (PA 6 and PA 6.6)	1.53	Paraloid F-10 (butyl methacrylate, 40% solution in mineral and aromatic solvent, 9 : 1)	1.49
High-density polyethylene (HDPE)	1.54	Methyl cellulose	1.50
Polyvinyl chloride (unplasticised, PVC-U)	1.54	HXTAL-NYL-1 (epoxide resin EP)	1.52
Polyester (PET)	1.55–1.64	Araldite 2020	1.55
Styrene-acrylonitrile resin (SAN)	1.57	Unsaturated polyester resin (UP)	1.54–1.72
Polycarbonate (PC)	1.59	Fynebond (epoxide resin EP)	1.57
Polystyrene (PS)	1.59		

Sources: O'Connor 2015; Lagana, van Oosten 2011; Rubin 1990; CAMEO: Conservation and Art Materials Encyclopedia Online, Museum of Fine Arts; Professional Plastics. Physical Properties of Plastics; Scientific Polymer Products Inc, Refractive Index of Polymers by Index.

Appendix 11. Worksheet for evaluating the condition of a plastic object

Location/institute	
Date	
Evaluator	

Code		**Photograph:**
Description		
Age		
Material(s)		
Measurements		
Previous repairs		

Mechanical damage	**Rating**	**Physical and chemical damage**	**Rating**	**Biological damage**	**Rating**
1. Scratches, friction:		1. hrinkage:		1. Traces of chewing:	
2. Soiling:		2. Light damage:		2. Damage caused by insects:	
3. Dents, deformation:		3. Thermal degradation:		3. Fungal damage:	
4. Cracks, holes:		4. Hydrolysis:		4. Other:	
5. Missing parts:		5. Oxidation:			
6. Other:		6. Solvent damage:			
		7. Plasticiser/additive migration:			
Overall score for damage:					
Score for object condition:					

EESTI RAHVA MUUSEUM
Estonian National Museum

ICOM international council of museums Estonia

ICOM international council of museums

CONSERVATION ICOM international committee for conservation