Deel 1: The material: silicone rubber

THE MATERIAL: SILICONE RUBBER

Silicone rubber belongs to the group of *plastics* or *polymeric materials*. Plastics have been produced since the nineteenth century. Between 1935 and 1945 many new polymers were introduced, among which silicones[1].

Monomers produce macromolecules by polymerisation, poly-addition and polycondensation. These polymers can be linear, branched or cross-linked. Plastics can be divided in *thermoplastics* and *thermosets.* Thermoplastics are linear or branched molecules. The molecules are held together by secondary bonds. The bonds can be easily broken by chemical or physical influences, e.g. solvents, water heat. This process is reversible. Thermosets are cross-linked molecules held together by primary or chemical bonds. Primary bonds can only be broken irreversibly.

Silicone rubber is an *elastomer*. Elastomers consist of macromolecules of which cross-linking is less frequent than other thermosets, with additional secondary bonds. Therefore they have rubber-like properties, but cannot be made plastic by heating. Silicon atoms form chains linking with oxygen atoms: Si-O-Si.
Silicone rubbers have a very low glass transition temperature (Tg) and are therefore likely to pick up and hold dirt particles. They are also electrostatic[2]. The cross-linked polymers can be swollen by solvents[3].

During production, stabilisers, anti-oxidants, UV-absorbers, dye stuffs, pigments, fillers, flame retardants, lubricants, impact modifiers, processing aid and plasticisers can be added to give the compound specific properties[4]. This results in a huge number of different plastics. To make identification even more difficult, the polymer industry changes the formulation of additives, but the trade name often stays the same.

Deel 2: Causes of degradation

CAUSES OF DEGRADATION

In order to slow down the rate of degradation it is necessary to understand the factors

1 Shashoua, 2001
2 van Oosten, 1999
3 Horie, 1987
4 van Oosten, 1999; Shashous, 2001

which initiate and catalyse the degradation process. The right conservation treatment and storage conditions can prolong the useful lifetime of the rubber moulds. In general, excessive exposure to light, heat, moisture, chemicals and gaseous pollutants reduce longevity of plastics. Both internal and external effects can initiate and catalyse the degradation of plastics.

Internal effects

Compounding

Degradation of plastics can be caused by the composition of the compound. One component will influence the rate and extent of degradation of others. Pigments containing metal ions may accelerate the degradation process. On the other hand, added stabilisers, UV-absorbers or anti-oxidants can inhibit the degradation process[5].

Plasticisers

The stickiness that some moulds show could be caused by plasticisers leaching out of the rubber. This will alter the composition, and therefore the properties, of the compound. The loss of plasticisers usually results in the plastic becoming dry or brittle. Stabilisers and other modifiers can also leach out of the rubber.

Glass Transition Temperature (Tg)

Low Tg and being electrostatic are the reason dirt and dust is attracted to and sticks on the surface of plastics. The leached out plasticiser also leaves a sticky layer on the surface to attract dirt and dust.

External effects

Light

Especially UV-radiation initiates the photo-oxidation and the cross-linking of plastic molecules. This is observed as fading and discoloration, embrittlement and cracking[6].

Air

Ozone and oxygen initiate and accelerate the oxidative degradation. Ozone has a specific and complete action on unsaturated organic compounds, that is to say it will break every double bond on a carbon chain with which it comes into contact. This destroys the material. In this way transverse cracks appear on rubber bands which then

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5 van Oosten, 1999
6 van Oosten, 1999

snap when stretched[7].

Relative humidity

High relative humidities cause a hydrolysis of ester bonds with some plastics[8]. Other plastics become dry when the RH is too low[9].

Dirt

The effect dirt has on objects is mostly physical, due principally to the addition of material rather than to changes in chemical composition. However, the presence of dirt or dust may accelerate some chemical changes[10]. A low glass transition temperature enables the polymer to absorb dirt[11].

7 Garry Thomson, 1978
8 van Oosten, 1999
9 P. Keune, College Kunststoffen, 2002
10 Ashley-Smith, 1999
11 Horie, 1987

Results of degradation

The degradation process can change the chemical composition of the plastics. Chemical analysis and identification of degraded plastics is therefore extremely difficult. The degradation process often has a long induction time without any signs of degradation yet. After that, the degradation process can go really fast.

Migrating components can be seen on the surface, sometimes causing stickiness. The plastic can become dry, brittle, matt, crackled or soft and sticky; the colour can fade or discolour. Dust can be attracted and the object can smell bad. The softness can cause deformation and loss of rubber-like properties.

Research

Substance leaching out of the rubber

It is important to know which substance is leaching out of the objects, what effect this will have on both the rubber moulds and the surrounding objects. Although loss of plasticisers usually results in dryness and brittleness, the moulds in the museum show no sign of these phenomena. They become more soft and sticky. It is important for the conservator to know whether this substance is toxic or not and whether its evaporation will influence the degradation of neighbouring objects. When the rubber is autocatalytic, the substance could accelerate the degradation process and it is therefore important to remove it.

Solvents

In order to find a method for surface cleaning it is important to test the different silicone rubbers found in the museum for their resistance to solvents and water.

Relative Humidity

The RH at which the rubber moulds should be stored (high, low or about 50%) needs to be tested.

Deel 3: Conservation

CONSERVATION

Passive Conservation

- *Light*

The moulds should not be exposed to too much light, especially UV-radiation. In general 50 to 300 lux is advised[12].

- *Relative humidity*

In general a RH of 55±3% is advised, but some plastics require a higher or lower RH.

- *Temperature*

High temperatures cause softening of plastics; a temperature of 18±2ºC is acceptable.

- *Storage*

Deformation of the moulds should be prevented. The moulds must be placed horizontally. The moulds should not be piled on top of each other.

- *Dust*

To prevent dust from contaminating the surfaces, the objects could be covered with acid-free tissue paper or unbleached cotton[13].

- *Registration*

The moulds should be registered, with a detailed description and a photograph. The process of casting moulds and their role in the minting process should be described.

Active Conservation

- *Surface cleaning*

The collection of rubber moulds need surface cleaning. The stickiness on the surface will have to be removed , together with the accumulated dust. Most plastics are sensitive to organic liquids, aqueous solutions and water itself, particularly if the polymer is deteriorated; therefore cleaning is difficult[14]. Cleaning methods for plastics are still poorly developed.

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12 van Oosten, 1999
13 van Oosten, 1999
14 Shashoua, 2001

Other methods used for conservation of plastics

- *Surface coating*

Applying coatings and paint are complex for technical and ethical reasons. Applying clear polyurethane coatings on a degraded polyurethane foam object caused a lot of practical problems[15].

- *Oxygen-free storage*

Another method to inhibit oxidation is to create an oxygen-free environment. This could be done by packing the objects in impermeable multi-laminate plastic bags with Ageless oxygen absorber sachets[16]. These sachets take the oxygen from the surrounding environment. The plastic has to be tested for its resistance to products leaching out of the object. A more thorough, but also more expensive, method is using glass flasks with Ageless oxygen absorber sachets and flushing them with N_2. Glass is perhaps the best material for both storage and display.

- *Ventilation versus micro-climate*

When the plastic emits vapours that cause damage to other objects, is toxic for the conservator or accelerates its own degradation process (autocatalytic), good ventilation is necessary.

However, in the case of PVC a glass jar or display case that is completely sealed off could be beneficial. In this case the air with emitted vapours becomes saturated and in equilibrium. The saturated air will prevent more vapours from coming to the surface and leaching out[17].

- *Cold storage*

In general the rate of a chemical reaction doubles if the temperature is raised by 15° C[18]. The use of a domestic freezer operating around -20°C is currently being researched for the storage of PVC[19]. This should slow down chemical reactions dramatically.

It will not be easy to pack the rubber moulds horizontally as efficient as possible in a freezer, but additional advantages are the lack of light and dust inside the freezer.

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15 Keneghan, Breen, 1999
16 Lecture Agnès Brokerhof
17 P. Keune, College Kunststoffen, 2002
18 www.natmus.dk/cons/lab/barbie/bb.htm
19 www.natmus.dk/cons/lab/barbie/bb.htm

Exhibition

The rubber moulds should be exhibited horizontally taking into account the above stated recommendations for light, temperature and relative humidity.

deel 4: Literatuur

BIBLIOGRAPHY

- Ashley-Smith, J., 'Risk assessment for object conservation', Butterworth-Heinemann, Oxford, 1999

- Engel, L. et al, "An atlas of polymer Damage", 1978

- Horie, C.V., 'Materials for conservation', Butterworth-Heinemann, Oxford, 1987

- Keneghan, B. and Breen, S., 'Plastics: identification, degradation and conservation', Modern Art: Who Cares?, (eds. U. Hummelen and D. Sillé) The foundation for the conservation of modern art Netherlands and Institute for Cultural Heritage, Amsterdam, 1999, pp 158-163

- Keune, P., College kunststoffen versie september 2002

- Keune, P., "Conservation part I", Reinwardt Academy, december 1994

- Oosten, T. van, 'Here today, gone tomorrow? Problems with plastics in comtemporary art', Modern Art: Who Cares?, (eds. U. Hummelen and D. Sillé) The foundation for the conservation of modern art Netherlands and Institute for Cultural Heritage, Amsterdam, 1999, pp 158-163

- Shashoua, Y. R., 'Inhibiting the deterioration of plasticized poly (vinyl chloride) – a museum perspective' PhD thesis, The Technical University of Denmark, The National Museum of Denmark (www.natmus.dk)

- Shashoua, Y. R., 'Degradation and inhibitive conservation of Baltic amber in museum collections', The National Museum of Denmark (www.natmus.dk)

- Shashoua, Y. R., 'Barbie gets cool!', www.natmus.dk/cons/lab/barbie/bb.htm

- Thomsom, G., ‘The museum Environment’, Butterworth-Heinemann, Oxford, 1978 (second edition)

- www.koninklijkenederlandsemunt.nl

- ICOM-CC working Group Modern Materials
  www.icom.org

- www.newzealandmint.com

- www.resource.gov.uk/information/advice/conserv11.asp

- “Some thoughts on the conservation of rubber products”, “Antidegradents – chemical protection for rubber articles”, “The ageing of rubber vulcanizates”
  www.bouncing-balls.com