## 3.6. Conclusions and outline of the further perspectives

There is no standard way how to protect and to prolong the remaining service life of damaged plastic items. Any attempt to slow down their deterioration often may cause more problems than doing nothing. At present, the most effective interventions are preventive, displaying at risk items in a cool, low light environment with stable humidity, for example. Other precautionary measures include using materials such as absorbents to scavenge oxygen or acidic fumes from the atmosphere surrounding the objects. As the recognition of polymer degradation improves, conservation guidelines are beginning to emerge. High tech solutions which could help in theory are prohibitively expensive, but tailor made scavengers such as activated charcoal or Ageless™ help to create a low oxygen environment. Ageless, is a scavenger of gaseous oxygen for treatment of individual specimens. It is composed of moist, active, iron oxide powder encased in a porous packet. Oxygen from the atmosphere penetrates the packet and further oxidises the powder. Ageless is normally used to prolong the shelf-life of dry foods by absorbing oxygen. Epoxidised soyabean oil has also been tested with encouraging results as an acid absorbing coating on degrading cellulose nitrate. Another possibility might be to use gamma rays to polymerize some monomers in fragile plastics such as polyurethane foam that is used in furniture cushions. The same technique could be used to form a protective veneer on some types of plastics.

The prolongation of residual service life of a given polymer in practical utilization has significant practical impact. Even though not all are applicable in prolongation of the service life of the museum artefacts, it is necessary to know about possible polymer stabilisation before the polymer is used in artifact. This is the only moment in the artifact future existence when its service life may be prolonged to hundred years or more (Grassie 1981; Matisová-Rychlá
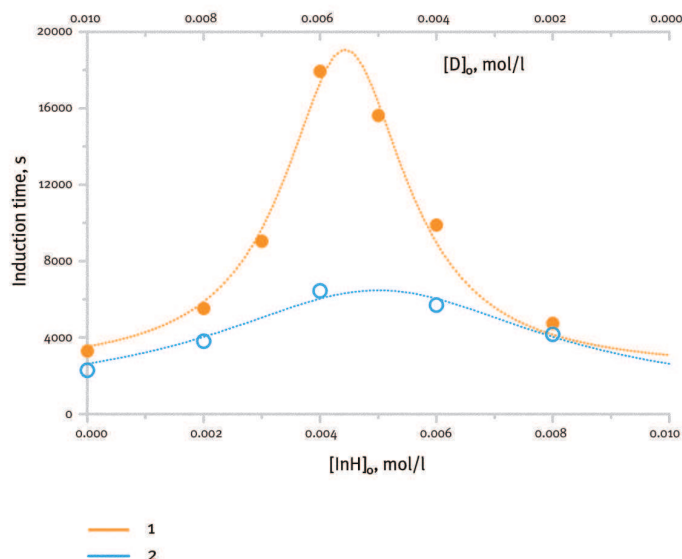
Figure 48. The theoretical plot of induction time of oxidation determined for wi=0, (zero rate of initiation according to reaction 1 of Figure 2) on composition of the mixture of inhibitors InH (chain breaking antioxidant) and D (peroxide decompose)r having the total sum of concentrations 0.01 mol/l. The curve 2 below is the plot of induction times for the same values of parameters as for line 1 but wi=5 10^{-8} mol/l. The initial concentration of hydroperoxides was 0.001 mol/l

1996; Rychlý *et al.* 2011). The routes how to achieve a longer service time of a material consist in modifying it by elimination of its weakest structural sites or in mixing a polymer with additives, which protect the polymer by reducing or eliminating active site production that lead to degradation pathways.

One important point should be emphasised here. The efficiency of any stabilising system depends very much on the removal or depletion of the defect structures in the original polymer. The example may be shown in Figure 48 where the induction time of oxidation for synergistic mixture is theoretically depicted. The line 2 shows that the effect of the synergistic mixture of two antioxidants on thermo-oxidation stability is negligible if there is a relatively significant initiation of oxidation reaction in a way independent from the route taking place via hydroperoxides.

This implicates that it is vitally important to avoid any recycled plastic when preparing new artefacts.

Protective additive or stabiliser functions by absorbing the energy of an initiation process more efficiently than the polymer itself. Once formed, the primary sites of degradation may be deactivated either physically (quenching of excited states) or chemically (inhibition of chemical reaction propagating the oxidation) (See e.g. reactions 14 and 15 of the Figure 2). The species which are formed from protective compounds should be less reactive than species being formed during degradation of non-protected polymer.

Since the deterioration of the polymer properties is related to the polymer degradation, the protective additives aimed at the increase of residual service life are called antidegradants or stabilisers. According to the predominating function of the above additives we distinguish thermo and photo oxidation stabilisers, antioxidants, antiozonants, flame retardants, antirads (radiation protectants), biological antioxidants, etc. In the mixture of different additives functioning as polymer stabilisers, the resulting effect may be either synergistic, when prolongation of the service life due to the mixture of stabilisers is higher than a simple arithmetic sum of each, or antagonistic when the mixture of stabilisers is less efficient than the sum of each of the component.

Stabilising additives for polymers usually scavenge free radicals or hydroperoxides from the system. The effect of such additives consists in reactions 14) and 15) of the Figure 2 which compete with propagation of free radicals according to reactions 3)-6). According to the predominance of reaction 14) or 15) we distinguish chain breaking antioxidants which intervene directly with the oxidation cycle by fast reactions with alkyl or peroxyl radicals (reaction 14) and

preventive antioxidants which impede formation of free radicals by the non-radical decomposition of hydroperoxides (reaction 15).

The most widely used antioxidants are sterically hindered phenols and bis-phenols; other additives are combined with phenols mostly in synergistic mixtures. Hindered phenols are remarkably efficient in protecting saturated hydrocarbon polymers against thermal oxidation. The fractions in the range of 100 – 1000 ppm of stabiliser are able to increase the induction time by one order of magnitude. The stabilisation mechanism and trends of structure – property relationships are generally well understood but quantitative (kinetic) approaches of the stabilisers efficiency are scarce and often based on simplifying hypotheses, for instance: the predominance of radical scavenging by the stabiliser in termination reactions, the stationary state assumption or the constancy of initiation rate (which is explicitly assumed or which derives from the steady state assumption). It appears generally difficult to explain the very high stabiliser efficiency in the frame of schemes where the rate of stabiliser consumption is expected to be equal (at least in a first approximation) to the initiation rate.

Several mechanisms of synergism for two different antioxidants were presented until now, namely:

- An interaction of both additives and formation of a new component which acts as more efficient stabiliser. Example: aromatic amines + mercaptobenzimidazol.
- A redox mechanism. Oxidised form of a more efficient component of synergic mixture is reduced by less reactive component. Example: aromatic amines + phenols.
- Co-effect of chain breaking antioxidants and chelating compounds reducing the rate of initiation by complexing transition metal ions and converting them to the less efficient initiators. The effect of annealing of stabilised polymer sample on prolongation of its induction period may be included here, as well, provided that hindered phenols react with transition metals converting them to less efficient initiators.
- Interaction of acceptors of reactive free radicals and compounds which suppress the transfer reaction of an inhibitor radicals with substrate as it occurs in the system of antioxidants and compounds with conjugated system of double C=C bonds.
- Synergism based on the mixture of chain breaking antioxidant (sterically hindered phenol) and hydroperoxide decomposer (organic sulfides or phosphites).

The search for synergistic mixtures of stabilisers is going on in application research with an emphasis on non-toxic and additives friendly to nature which are well compatible with a given polymer.

Proper selection of testing conditions revealed an outstanding efficiency of hindered amine stabilisers [HAS] in the temperature range bellow 130°C as the long term heat stabilisers. An efficient component of the stabilising system, sterically hindered nitroxide radicals, similarly as in the light protecting action, are supposed to capture alkyl radicals to give hydroxamic acid ethers which in reaction with peroxyl radicals give back nitroxides. The rate of the former reaction is so high that it is capable of competing with reaction of alkyl radicals and oxygen (reaction 5 of the Figure 2).

What to do with plastics already used in artefacts? Even though this subheadings is not directly related to the results we feel that it should be of use for the further treatments of potentially degrading plastics. Cellulose acetate should be displayed and stored under ventilated conditions or with ethanoic acid scavengers if stored in unventilated enclosures. Cellulose acetate objects should not be stored in enclosures with, or in proximity to, acid sensitive (particularly ethanoic acid sensitive) materials such as metal, textiles, and paper. The main conservation strategy for cellulose esters is to reduce exposure to moisture, primarily by reducing relative humidity. Reducing temperature is also effective, since, in common with all chemical reactions, decreasing the temperature decreases the rate of degradation reactions. Reduced temperature also reduces the rate of plasticiser loss and retains plastic flexibility although the plastic may be less flexible at the reduced temperature. It is also essential to ensure that there is adequate ventilation to remove harmful gaseous degradation products to prevent damage to objects in the vicinity. Objects that are heavily degraded or in the process of degrading rapidly should be removed and segregated from the rest of the collection. Enclosures (drawers, cabinets, display cases, etc.) that contain cellulose nitrate should be well ventilated to prevent buildup of acid vapors. Special storage conditions and locations should be considered for cellulose nitrate, including cold storage. Cellulose nitrate plasticised with camphor (e.g. celluloid) which material sublimes from the plastic, causing the object to become more brittle and to shrink. The shrinkage tension set up in the brittle plastic often leads to severe cracking or crizzling. This problem may not be so severe in cellulose nitrate plasticised by materials other than camphor which are less volatile.

The greatest problems with poly(vinyl chloride) are related to the additives. Migration of plasticiser and other additives creates accretions on the poly(vinyl chloride) surface. These deposits of additives on the surface of the plastic, called bloom, can seriously stain or corrode the surface of other materials they contact. It was found that plasticiser

bloom will form if the plasticiser content is more that 30% of the poly(vinyl chloride) weight and that phthalate ester plasticisers can hydrolyze to form crystals of phthalic acid and phthalic anhydride. The bloom can be removed by wiping or mild solvent treatment (not recommended), but usually returns. Formation of bloom is driven by an inherent incompatibility between the plastic and the additive. The presence of bloom on the poly(vinyl chloride) is not damaging to the poly(vinyl chloride), although it does indicate that the poly(vinyl chloride) is degrading. It need not be removed if contact with other objects is prevented by shields, interleaves, and packaging. Although poly(vinyl chloride) is susceptible to degradation by light and heat, this is not usually the most serious problem in museums. Manufacturers presently control this by adding light and heat stabilisers. Unfortunately these stabilisers are consumed as they do their job, until at some time the stabilisers are exhausted, and additional exposure suddenly results in deterioration. Thus a poly(vinyl chloride) object that has been surviving nicely under lights for several years may suddenly begin rapid deterioration. This was a common scenario for the vinyl roofs on cars. They would be in good shape for several years then suddenly rot away. In experiments on poly(vinyl chloride) degradation dehydrochlorination has not been detected in the dark after six months. However in accelerated ageing experiments dehydrochlorination did occur but incorporation of zeolites or epoxidised soya bean oil (ESBO) inhibited the discoloration of poly(vinyl chloride) caused by dehydrochlorination. The use of zeolite pellets in storage boxes containing poly(vinyl chloride) objects to inhibit discoloration is very recommended.

Since oxygen is present in the atmosphere, oxidative degradation can be stopped also by placing the plastics such as polyurethanes into an oxygen free enclosure. This so-called anoxic storage requires that the object be sealed into a package where there is no ventilation. This exacerbates degradation if the degradation products catalyze degradation, so sealing degrading plastics into packages must be very carefully tested and monitored. Although avoiding exposure to light may slow oxidative degradation, degradation will not stop in the absence of light (Kerr 1993). There are many examples of polyurethane foams used for supporting objects in dark storage drawers that have completely degraded to powder. Recommended environmental conditions for polyurethanes are typical for textiles, with good ventilation to remove volatile degradation products. Also, there should be no contact between polyurethane objects and other objects, including other parts of the object itself, to prevent sticking. Silicone and PTFE coated fabrics have been used as nonstick interleaves.

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