

Conservation of Rubber

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Since the 1930's at least, museums and similar organizations have been concerned with acquiring and displaying articles of social history to provide a long-term record of our cultural heritage. Unfortunately this conflicts with the very nature of many modern articles which are designed to be ephemeral. Artists, always searching for new materials through which to express themselves, have used natural rubber latex as a painting medium whilst latex sheets or latex-coated fabrics have been used as materials on which to paint or from which to create sculptures. The rapid degradation of these artworks gives considerable cause for concern.

The conservation of rubber artefacts, and rubber in artefacts, is thus fundamental to any programme designed to preserve the cultural heritage, and within this scenario there are three questions to be asked: what is causing the damage, what can be done to reverse damage already suffered by older objects, and what can be done to the more modern items, including those acquired new, to ensure that they are stored and displayed under optimum conditions and given any treatment appropriate to prolonging their display and storage lives.

The answer to the first question is simple: [oxygen and/or ozone](#) (possibly catalysed by light, heat or pro-oxidant metals) but the next two questions cannot be answered so easily.

Unlike the rubber product manufacturer, who can formulate his product to optimise its service life - which may not be very long - the conservator can only take the finished article and consider his or her options. These are Stabilization - holding the status quo short-term by limiting existing degradation chemistry - followed by Conservation - treating the stabilized article so that long-term degradation is minimised. The latter can entail anything from Consolidation - very limited (often invisible) reinforcement of the article through Restoration - treatment which could extend from consolidation to virtual Replication.

Within these options the conservator is governed by a series of guidelines which are based on the concepts that between stabilization and replacement as little as possible is actually done to the article and that whatever is done should be anachronistic. The former is intended to preserve as much of the original article as possible and the latter to enable repairs to be obvious to the expert but invisible to the layman if conservation records are lost. An obvious (quite genuine) example of the latter is the repairing of an 19th Century diving suit with water-soluble glue. As a final restriction, all conservation should be reversible in case better techniques are developed in the future. Not surprisingly these criteria often cannot be met and a compromise must be sought.

An historical lack of awareness of the problems likely to accrue from the collection of ephemera has now resulted in a vast back-log of valuable objects which require stabilization and/or conservation as a matter of extreme urgency whilst in the field of rubber conservation there is one overriding additional problem. 'Rubber', through common usage, has become a generic term. It covers a multitude of different elastomers, [natural](#) and the [synthetics](#), with different additives included for specific purposes, and with no obvious way, short of analysis, of distinguishing between either the additives or elastomers used.

It is revealing to consider the first 'port of call' for a conservator seeking any information - the 'Conservation Information Network' - a computerised database operated by the J Paul Getty Trust. A simple search for 'rubber' and 'conservation', carried out in late 1993, generated 122 references but, on reading through the abstracts, it became obvious that most were concerned with the use of rubber, in various forms, in conservation. Only 15 were actually related to the conservation of rubber (as well as one to ebonite).

What can be done to protect articles which are socially significant? Whatever scientific approach is adopted, it must go some way towards meeting the philosophical requirements of the museum and will depend on the reason for the conservation and the attitude of the person responsible for the conservation.

There is no single answer since there is no single material. The article for which conservation is being sought could be large and black or light coloured and very thin. Existing historical artefacts could be unvulcanized whilst modern materials could consist of a range of polymers, cure and protective systems, and fillers. However, in all cases there are only the options of leaving well alone, adding protective agents, coating the product with an impermeable membrane and/or removing the cause of the trouble - generally oxygen. For indoor collections ozone, light and temperature are usually under control although they will not be so for outdoor exhibits. Stress should also be considered. None of this will stop the [sulphur chemistry](#) continuing but this will not, by itself, harm the exhibit for several centuries.

It should also be realised that for modern black vulcanizates of reasonable bulk which are being stored or displayed under ambient conditions, the ingress of oxygen is limited and, apart from the surface few millimetres or so, the bulk rubber will remain in excellent condition for display purposes almost indefinitely.

If the decision is taken to chemically treat the article, then a choice of **protective agent** must be made and the conservator has but two approaches, either to diffuse the chemical into the rubber or to build up a protective surface coating. Before considering these alternatives, he or she must understand that antidegradents can operate by physical (barrier) means, chemical reactions or both. It is crucially important to understand which antidegradents work in which ways and what limitations they have.

Para-phenylenediamines (PPD's), added during manufacture, function both as antiozonants and antioxidants and they operate by reacting more readily than the rubber double bonds with any ozone present at the surface of the article. In so doing they build up a protective film which, as it thickens by continuing migration and further reaction of the migrated antiozonant, eventually provides an impermeable barrier to the gas. Any damage to the skin, such as by cracking, is repaired by further migration. There are many different PPD's and one of the main reasons for selecting a particular one is its solubility and rate of migration in the polymer system being protected, crucial parameters for long-term protection. PPD's oxidize to blue/purple/black materials and readily stain so their use must be selective.

Phenolic antidegradents are only antioxidants and have virtually no antiozonant activity. When oxygen attacks a rubber molecule various chain reactions occur which may result in both polymer chain breakage and the insertion of further crosslinks. The phenolics offer an alternative pathway in the chain reaction sequence and thus stop it progressing. It is essential to realise that they do not stop the initiation step so their effect is, at best, to slow down the oxidative breakdown, perhaps by up to five times. They do not form a protective 'skin' if oxidized on the rubber surface and need to be intimately dispersed/dissolved in the rubber to function. It is, however, possible for a protective skin of oxidized rubber to form under certain conditions.

Any physical barrier will stop or reduce oxygen and ozone diffusion into the rubber and might or might not crack depending on its brittleness and the mode of display or use of the article. Any subsequent capacity for self-healing will depend on whether there is more suitable material which can migrate from the bulk, of the article or whether the barrier material is present only as an added surface layer.

As long ago as 1931, Semon, Sloan and Craig reviewed proposals, published over the previous fifty years, to give protection to objects made without added antidegradents by topical application of protective agents dissolved in a solvent. Under their accelerated ageing tests some benefit was found but the protection was not long-term. Today, some conservators still advocate this approach, using a solvent for the antidegradent which will swell the rubber and thus facilitate diffusion into its bulk. This may not damage a new vulcanizate, although why one should wish to treat it in this way is not obvious, but, if the object is not vulcanized, or is degraded so that the surface is structurally weak, the rubber will either dissolve, or swell to such an extent that the surface will be severely damaged whilst damage could also be done to the bulk rubber vulcanizate, particularly since the solvent will be extracting whatever it can from within the vulcanizate whilst the antidegradent is diffusing in. If one really wishes to use this method, then a non-solvent for the rubber must be a better choice as this will still allow diffusion into the bulk rubber without appreciably swelling and damaging the surface structure. It might still, however, extract previously added materials from the article to its subsequent detriment.

If the choice is not to diffuse protective chemicals into the unprotected rubber, there is still the option of adding a protective surface coating, and such a skin can be built up by topical application, provided the limitations to crack repair and surface finish are appreciated.

One barrier technique has been well established for many years and is the coating of the article with an oil lacquer which is then vulcanized. A possible modern equivalent procedure might be the use of a prevulcanized butyl latex spray-coat since butyl rubber is relatively impermeable to air.

The ultimate barrier layer must be an enclosed vessel which can be filled with an inert gas but, even then, the choice of the material from which to construct the vessel is not always obvious as many plastics themselves decompose all too rapidly. Simple plastic bags are readily permeable to air but there are now virtually impermeable multi-laminate ones which, unfortunately, are not suitable for display purposes although they could be used for long-term storage. Perhaps glass is the best material for both storage and display but nothing will reverse degradation which has already occurred.

A final point should be noted about the temperature of storage. Many raw and lightly vulcanized rubbers crystallise at low temperatures and, particularly with old samples of natural rubber, this phenomenon can be confused with oxidative brittleness. Although the temperature for the maximum rate of crystallization of natural rubber is -26°C , it will crystallize slowly at cool room temperatures ($10 - 15^{\circ}\text{C}$) but then has the peculiar property that it can only be melted by heating to about 30°C above the temperature at which crystallization took place. An article which has undergone long-term storage in a

freezer will therefore thaw quite quickly when brought to normal ambient temperature but if a similar article has been stored in a refrigerator at, say, +5°C it will remain brittle until it has been warmed to 35 - 40°C. The thawing takes place in a matter of seconds or minutes for thin articles, depending only on the transfer of heat through the bulk so any rubber article which has become brittle after prolonged storage should be warmed briefly to see if it will regain its elasticity. If the article has become brittle through oxidation, this will do no further significant damage!