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1 OF 1

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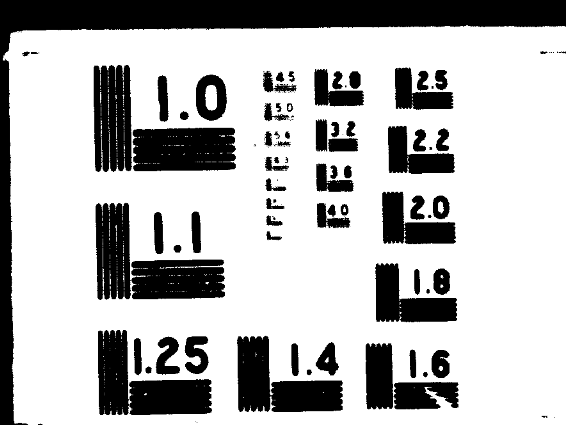

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PROBLEMS OF PLASTICS DETERIORATION IN BUILDING IN TROPICAL AREAS

by

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Chapter 1

Introduction

The fact that plastic materials were susceptible to biological attack and breakdown became evident during the second world war. Up to that time plastics had their greatest usage in temperate regions of the world with little evidence of biological attack. During the second world war however, large amounts of plastic-containing equipment were moved into tropical regions of the world; areas, which because of their high ambient temperatures and high humidities, were more conducive to large scale biological attack.

This discovery lead to the initiation of intensive research programmes, initially by government departments, but much of this earlier reported work tends to be confusing, little distinction being made between the susceptibility of the polymeric constituents and the plasticisers, fillers etc., or whether, in fact, microorganisms found on the surface of a plastic were responsible for breakdown of the plastic.

In spite of this earlier confusion several general principles emerged from the research:

(1) That the polymeric constituents of plastics, in general, were resistant to microbiological attack.

(2) That organic additives to plastics were susceptible to microbiological attack.

We must stress at this point the importance of the fungi and the bacteria in the breakdown of plastics. Degradation by the fungi appears to be of most importance, high relative humidities (80 - 100%)

and temperatures (30°C) being favourable for their growth. The bacteria appear to be less important in plastics degradation but their probable synergistic relationships with the fungi must not be overlooked. Bacteriological degradation of plastics is an important factor when plastics are buried in the soil or when immersed in water. To a lesser extent plastics are susceptible to localised mechanical damage through the gnawing activities of termites, insects and rodents, and by the boring activities of molluscs.

The principles behind the biodeterioration of materials were outlined by Hueck (1) and for plastics can be summarised as follows:-

1. Staining - superficial growth of microorganisms rendering the materials unusable.
2. Discolourations - caused by actual attack on the plastic by the microorganism or by chemical excretions of the microorganism.
3. Pitting and blistering - of the surface of a plastic by the activities of bacteria and fungi.
4. Lesions - undefined (localised) parts of a plastic material being gnawed or broken away by the activities of termites, insects and rodents.

The above " morphological " symptoms can lead to undesirable changes in the properties of plastics:

(a) Changes in mechanical properties - loss in weight, changes in tensile strength, elongation and flexibility.

(b) Changes in electrical properties - in the conductivity of insulating materials attacked or invaded by fungi.

(c) Changes in optical properties - in the opacity of clear-type plastics by the etching activities of fungal overgrowth.

(d) Changes in chemical properties - breakdown of plasticisers, fillers etc.

The scope of the problems facing plastics manufacturers can be seen from a survey of The Biodeterioration of Plastics:

(a) Attack by Insects and Rodents.

The attack of P.V.C. cable coatings by termites is well documented although the plastic itself does not seem to form a foodstuff for the termites. Snyder (2) states that the only plastic which he has tested which has not been attacked by termites is cellulose acetate. It appears, from the literature, that termite attack on underground plastic cables is brought about simply because the cable is " in the way " of burrowing activities, or if the plastic has been in contact with food detritus which would attract the termites (3) (8). The red ant (Monomorium destructor) has been reported to attack polyethylene (4) (7) and P.V.C. cable coatings (5), in the latter case causing frequent electricity failures; and the carpenter ant has been reported to attack polyethylene cables (3). The larva of the false clothes moth (Hofmannophila pseudospretella) is known to eat its way through polyethylene, polystyrene and nylon; and the larvae of aquatic moths have been found damaging polyethylene linings to ponds, eating their way through the polyethylene to attach themselves to the rougher surface beneath before pupating (6).

Rodents, particularly rats and squirrels, will gnaw through any type of plastic pipe or cable coating if it obstructs their access to food or their burrowing activities. Recent work has also shown that male rats will gnaw through several types of material, including plastics, if that material forms a barrier between the male rat and a sexually receptive female rat (9)

(b) Microbiological attack

It is generally agreed that the majority of synthetic polymers are resistant to microbiological degradation (10) (11) (12) (13) (14) although little information which clearly relates to the susceptibility of polymers is to be found. The chemically reactive groupings present in high molecular weight polymers are inaccessible to microbial attack due to high intermolecular forces. The only polymers to date which do show signs of susceptibility to microbial attack are melamine - formaldehyde, cellulose nitrate and polyvinyl acetate (10) (15). The resistance of polymers to microbial attack is indicated in Table 1. adapted from Wessel (10) :-

Polymer	Resistance	Polymer	Resistance
Polymethyl methacrylate	Good	P. C. T. F. E.	Good
Polyacrylonitrile	Good	Polypropylene	Good
		Polyisobutylene	Good
Cellulose acetate-butyrate	Good	Polycarbonates	Good
Cellulose acetate-propionate	Good	Polystyrene	Good
Ethyl cellulose	Good	P.V.C.	Good
		Vinyl chloride/ vinyl acetate copolymer	Good
Phenol formaldehyde	Good	Polyvinylidene chloride	Good
Urea formaldehyde	Good	Polyvinyl butyral	Good
Nylon	Good	Epoxies	Good
Polyethylene	Good	Chlorinated polyethers	Good
P.T.F.E.	Good		

Table 1

Microbiological resistance of polymeric constituents of plastics.

Difficulties involved in assessing the susceptibility of a polymer to microbial attack include the extreme slowness of possible degradation reactions and suitable methods for measuring these.

found in the urine of animals implanted with labelled polymers (16), implying a biochemical breakdown of the polymers. These experiments must not be overlooked, neither must experiments by Mills and Eggins, 1970 (17) in which chemical oxidation products of polyethylene were shown to be microbiologically degradable. In fact the whole field of physico/chemical attack on the polymer forming products which might be susceptible to biological attack has still to be explored.

In general however, we can state that the majority of polymers are inherently resistant to microbiological attack.

Processing ingredients

The plasticisers, as a group of low molecular weight compounds (relative to polymers), influence the susceptibility of a plastic to microbial attack. Removal of the plasticiser by microorganisms leads to undesirable changes in the properties of the plastic which in turn lead to a physical weakening of the plastic; loss of antioxidants, stabilisers etc., would render the polymer susceptible to physico/photochemical breakdown rendering the material (if load bearing) mechanically unsound.

Although the cellulosics were the first plasticised plastics it is estimated that the majority of plasticisers now produced are used by the vinyl industry (18). Chemically they are high boiling organic compounds, usually liquid, and predominantly esters of organic acids or phosphoric acid. Others are hydrocarbons, halogenated hydrocarbons, epoxides, ethers and various polymers (18). A large number of plasticisers will support microbial growth and are able to be broken down, to a greater or lesser degree. A list of biodegradable plasticisers is presented in Table 2; this list has been based on the one produced by Heap (19) in 1965 and includes many plasticisers which have been reported to be degradable since 1965. Where any doubt exists in the literature as to whether a particular plasticiser is degradable or not, it has been placed in this table of biodegradable plasticisers (which accounts for the inclusion of some phthalic acid derivatives, the whole class of which are amongst the most resistant type of plasticiser).

Table 2: Biodegradable Plasticisers

Hydrogenated methyl abietate
Tri-n-butyl aconitate
Triethyl aconitate
Adipic acid ester P 103 N
Adipic acid ester P 204 N
Butylene glycol polyadipate
Di-isodecyl adipate
Di-isooctyl adipate
Di-(1,3 dimethyl dibutyl) adipate
Di-hexyl adipate
Di-iso-octyl azelate
Di-(ethylene glycol monobutyl ether) - azelate
Benzyl benzoate
Chlorinated hydrocarbons : Aroclor 1254 : Aroclor 1263
Glyceryl triacetate
Diethylene glycol ethyl ether acetate
Diethylene glycol butyl ether acetate
Ethyl phthalyl ether glycolate
Methyl phthalyl ethyl glycolate
Methyl phthalyl methyl glycolate
Butyl phthalyl butyl glycolate
Butyl laurate
Ethylene glycol laurate
Ethylene glycol ethyl ether laurate
Diethylene glycol monolaurate
Diethylene glycol ethyl ether laurate
Glyceryl laurate
Sorbitol laurate
Dibutyl ammonium oleate
Ethylene glycol methyl ether oleate
Nitrile from oleic and linoleic acids (N.T.D. - 181.5 - B)
Sorbitol oleate
Dipentaerythritol hexapropionate
Pentaerythritol diacetate dibytyrate
Pentaerythritol diacetate dipropionate

Pentaerythritol monoacetate tripropionate
Pentaerythritol triacetate monopropionate
Pentaerythritol tripropionate monomyristate
Pentaerythritol tetrabutyrate
Pentaerythritol tetrapropionate
Citric Acid tributyl ester
Triethylene glycol dipelargonate
Polymerio " Hexaplas " (I.C.I.) polypropylene adipate, end stopped with laurate
Acetyltributyl citrate (Pfizer Citroflex A4)
Epoxy plasticiciser (Estabex 2307)
Alkyl ester of mixed dibasic acids
Triphenyl phosphate
Diphenyl mono-(p-tert-butyl phenyl) phosphate
Monophenyl di-(p-tert-butyl phenyl) phosphate
Diphenyl mono-o-xenyl phosphate
Tri-(2-nitro-2 methyl propyl) phosphate
Tricresyl phosphate
Tri-2-ethyl hexyl phosphate
Hexyl phosphate
Diamyl phthalate
Dicapryl phthalate
Diphenyl phthalate
Ethyl-2-methyl-2 nitropropyl phthalate
Butyl isodecyl phthalate
n-octyl n decyl phthalate
iso-octyl iso-decyl phthalate
octyl phthalate
Methyl acetyl ricinoleate
Butyl acetyl ricinoleate
Ethylene glycol methyl ether acetyl ricinoleate
Glyceryl monoricinoleate
Glycol sebacate resin
Sebacic acid alkyd resins - Paraplex G 25
- Paraplex RG 2
- Paraplex RG 20
- Paraplex X - 100
Ester type alkyd resin - Duraplex C 50 LV
Sebacic acid ester P 204 N
Di-2 ethyl hexyl sebacate
Di-iso-octyl sebacate
Polymeric Rheoplex (Geigy) polypropylene sebacate
Dimethyl sebacate
Dibutyl sebacate
Di-(1,3 - dimethyl butyl) sebacate
Di-(2 - ethyl hexyl) sebacate
Stearic Acid
n - butyl stearate
Cyclohexyl stearate
Butoxy ethyl stearate
Diethyl glycol ethyl ether stearate
Tetraethylene glycol monostearate
Tetraethylene glycol distearate

Fatty acid dimethyl amide (Plasticiser 35)
Triethyl tricarballylate
Tri-n-butyl carballylate
Tung oil
Castor oil
Cotton seed oil
Dehydrated castor oil
Refined Tall oil (Indusoil)
Triethanolamine dicaprylate
Epoxidised soya bean oil G 62/Di-iso-octyl phthalate 15/35 mixture
Epoxyester E D 3 (Lankro)/Di-iso-octyl phthalate 15/35 mixture

---

Table 2.

Biodegradable Plasticisers.

Many of the above plasticisers were tested in liquid form as the sole source of carbon in a microbiological medium. Monocultures and mixed cultures of fungi and bacteria were used as inocula and growth of these organisms upon the plasticiser was taken as an indication of breakdown of the plasticiser. In some cases chromatography, spectroscopy and other physical methods were used to establish the breakdown of the plasticiser (18). In some cases the plasticiser was incorporated into a P.V.C. mixture and the plastic strip was subjected to the activities of microorganisms, using pure cultures, polycultures and soil burial tests. Subsequebt breakdown in mechanical properties of the test strips gave an indication of the breakdown and removal of the plasticisers. It seems reasonable to assume that plasticisers which are susceptible to biodegradation in their liquid form would be susceptible when incorporated into a plastic material.

Since thermoplastic resins not containing plasticisers are generally resistant to attack by microorganisms it might be anticipated that internally plasticised polymers should be resistant also. This was confirmed by Stahl and Pessen (20) the results of which are shown in Table 3.

Polymer Trade Name	Composition of Polymer	Test results Shake Flask	Soil burial	Other methods
Kel - F	Monochlorotrifluoroethylene	R(G)	-	-
KF - VF 2	50% Monochlorotrifluoroethylene 50% vinylidene fluoride	R(G)	-	-
Nylon 66	Hexamethylenediamine, adipic acid	-	R(C)	R(C,N)
Polythene	Ethylene	R(G)	-	R(N)
Saran 115	85% Vinylidene chloride, 15% Vinyl chloride	R(P)	R(F)	-
Teflon	Tetrafluorethylene	R(Sh)	-	-
Tygon	Vinyl chloride, vinyl acetate	R(G)	-	-
Velon	Vinylidene chloride, small amount of vinyl chloride	-	-	R(N)
Vinyon	90% vinyl chloride, 10% vinyl acetate	R(F)	-	R(N)
0-123-184 (ERRL)	Vinyl stearate	R(G)	-	-
0-147-79-4,5 (ERRL)	55% Vinyl stearate 45% Vinyl chloride	R(G)	-	-
0-147-53-3 (ERRL)	30% Vinyl stearate 70% Vinyl chloride	R(G)	-	-

R = resistant, C = Cloth, F = Fibre, G = Granules, P = Powder,

Sh = Shavings, N = Not specified.

Table 3

Fungus susceptibilty of internally plasticised resins.

There appears to be no reported evidence of microbial breakdown of accelerators and antioxidants which are also incorporated into plastics formulations. The little evidence on accelerators for rubber (21) showed that the accelerators, in the normally applied amounts, would not prevent deterioration of the rubber and hence were not biocidal in properties. The usually small amounts of accelerators and antioxidants in plastics however would seem to preclude them as a major substrate for biological attack.

The facts presented in this chapter outline some of the problems facing plastics manufacturers having to produce a plastic material for use in tropical regions of the world. Biodeterioration is a problem which must be faced in such regions if the plastic produced is to be effective and retain its inherent properties. The requirements of plastics materials in Tropical areas, in light of the above evidence on biodeterioration, should be :-

(1) Good resistance to mechanical damage by insects, termites, ants, rodents etc.

(2) Resistance to chemicals excreted by organisms living on detritus lying on the surface of the plastic.

(3) Resistance to biochemical attack (biodeterioration) by microorganisms.

(4) Resistance to physico/chemical attack caused by U/V components of sunlight and atmospheric oxidation leading to the breakdown of the polymer and to possible biological attack.

Points (1) (2) and (3) can be achieved by using a plastic which contains no plasticiser or is internally plasticised; or which has incorporated in its formulation a selective repellant or biocide. Point (4) is outside the scope of this report but we feel that it is an important point which must not be overlooked when selecting plastics for use in tropical areas.

Chapter 2.

The Control of Biodeterioration.

It is to be expected that plastics containing susceptible polymers and/or plasticisers would become liable to deterioration in properties in a tropical environment i.e. an environment where temperature and humidity are optimal for fungal and bacterial growth. To summarise the expected behaviour of various plastics subjected to tropical exposure :-

Polyethylene, Polypropylene.

Resistance to biodeterioration (microbiological) is excellent. Surface growth of organisms on detritus lying on the plastic can be wiped off completely with no effects upon the physical properties of the plastic. This plastic, as with all others, is not immune from mechanical attack however, by insects, termites, rodents etc.

Polytetrafluorethylene.

P T F E shows excellent resistance.

Polyvinyl chloride.

The P.V.C. polymer itself shows good resistance to biodeterioration and it is to be expected that unplasticised or rigid P.V.C. would be resistent to microbial attack. However P.V.C. plasticised with a susceptible plasticiser will allow fungal and bacterial attack, with subsequent loss in properties of the P.V.C.

Polyvinyl alcohol.

This plastic is reported to be resistant to moulds and bacteria.

Polyvinyl acetate.

Both the polymer (15) and the plasticiser used in this plastic are susceptible to microbial degradation.

Polyvinylidene chloride.

This plastic appears to be resistant to fungi.

Polyvinyl butyral.

Its resistance depends upon the plasticiser used.

Polystyrene.

Good resistance, surface growth can be wiped off completely.

Polymethyl methacrylate.

The polymer is resistant, but plasticisers used with it can be susceptible.

Nylon.

Nylon is reported to be resistent to direct microbial attack but there is evidence that waste metabolites excreted by microorganisms can cause a chemical attack on the polymer with some loss in tensile properties (22). The monomeric constituents of Nylon - 6 can certainly be utilised by bacteria (23).

Cellulose plastics.

Cellulose acetate, cellulose acetate-butyrate, cellulose propionate, ethyl cellulose and benzyl cellulose are all fairly resistant to attack although their susceptibility varies with the plasticiser used. Cellulose nitrate is susceptible to attack.

Phenolic resins.

Phenolic resins show very good resistance to attack, the only susceptibilty being with the fillers used. If inorganic fillers are used then resistance is excellent. Any surface growth can be wiped off completely with no change in properties of the plastic.

Amino plastics.

Melamine formaldehyde resins do show susceptibility and this varies also with the fillers used. Aniline formaldehyde and urea resins are more resistant but resistance is lost if the resin is filled with organic fillers. Any surface growth can be wiped off.

Glass reinforced polyesters.

Resistance varies with the polyester used but good resistance has been reported (24).

The above survey of some of the plastics in general use today indicates the need for the inclusion of either resistant plasticisers into the plastic or the need for a protecting agent which will be actively biocidal against fungi and bacteria and hence protect the polymer and/or the plasticisers from microbial attack. If a resistant plasticiser cannot, for technical reasons, be incorporated into a susceptible plastics formulation, then a biocide must be used. The biocide must be carefully chosen, it ideally must have the following properties :-

(1) A broad spectrum of activity i.e. must be effective against fungi, bacteria and perhaps algae.

(2) High toxicity to organisms, but low toxicity to humans and animals.

(3) Low cost.

(4) Stability in use eg. against leaching by rainwater, degradation by high (tropical) temperatures.

(5) Be permanent and compatible with all the other components of the plastic.

Biocides for use against insect (termites, ants etc.) attack are usually of the repellent type and can either be incorporated into the plastic, painted over the surface, or incorporated into the environment around a plastic (e.g. in the soil). Insecticidal biocides for use with plastics are presented in Table 4.

Compound	Comments
Gammexane	May cause disintigration of soft grades of polyethylene. Not totally effective as an insecticide (7).
Aldrin, Dieldrin.	Effective when added to soil around a plastic. Also in P.V.C. (27).
Halowax	Chlorinated naphthalene
Hycol	Emulsified coal tar acids, coating materials.
Palum	Creosote oils, coating materials.
Pentachlorophenol compounds	Both coating materials and can be incorporated into P.V.C.
D.D.T. based compounds	Can be coated or incorporated into the soil. (Pollution hazards though)
Metal naphthenates (26)	0.1 to 10% incorporation in polyethylene.
N - alkylcaproanilides (25)	Act as plasticisers in P.V.C. and copolymers, toxic to insects and fungi.
N - substituted carbamates (28)	For incorporation in polyethylene, polypropylene and P.V.C.
1,2,4,5,6,7,8,8-octachloro - 4, 7-methano 3 alpha, 4, 7, 7, -alpha tetra-hydroindene (29)	Termite and ant killer. With most polymers and plasticisers.
o, o-diethyl-o-(2 isopropyl 4 methyl 6 pyrimidinyl) phosphorothioate (29)	Insecticide as above.
dichlorodiphenyl trichloroethane (29)	Insecticide, as above.
N, N' - diethyl toluimide (29)	Insect repellant, as above.
Phostoxin (30)	Insecticide - in soil around the plastic

Table 4.

Insecticidal biocides for plastics.

The above list is by no means complete but represents a cross section of some of the insecticides which have been used with plastics.

Protection against rodents can be achieved by using metal sheathings around the plastic pipe or coating or by the use of a rodenticide. Unfortunately rodenticides can be incorporated into plastics only when changes in colour and appearance of the plastic are secondary. Also objectionable odours are released by these compounds.

One compound, actidione, 3 - (2-(3, 5-dimethyl-2-oxocyclohexyl)-2-hydroxyethyl) glutarimide has been shown to stop all rodent attacks under both laboratory and simulated field conditions (31). Tests have revealed that many amines were repellent and the activity was enhanced through the presence of nitro groups; the aniline and O-anisidine derivatives of trinitrobenzene were particularly effective.

Other rodenticides include Zinc dimethyldithiocarbamate - cyclohexylamine complex (Z.A.C.), tetramethylthiuram disulphide and hexachlorophene. Z.A.C. is suitable for use in P.V.C., vinyl chloride copolymers, polyethylene and polyisobutylene (32); cyclohexenedicyclox-imides (33); compounds related to acrylamide (34) and Warfarin compounds, although rat resistance to Warafin is now known to have a genetic basis and hence can be passed on from parent to offspring (35).

When we come to consider the protection of plasticisers we are faced with two alternatives :

(a) to incorporate a non degradable plasticiser into the plastic; this might not be possible for some plastics since specific qualities produced by a susceptible plasticiser might not be produced by a non susceptible plasticiser;

(b) to incorporate a biocide along with a susceptible plasticiser to give protection against microbial attack to the plasticiser.

If we consider these points in turn; plasticisers claimed in the literature to be non degradable are listed in Table 5.

Table 5. Non degradable plasticisers.

Abietic acid
Dimethyl adipate
Di (2 - ethylhexyl) adipate
Monochloroacetic acid
Di (2 - ethylhexyl) azelate
Ethyl-o-benzoyl benzoate
Chlorinated diphenyls : Aroclor 1242
Aroclor 1248
Aroclor 1262
Aroclor 1270
Aroclor 5460

Clorowax
Cerechlor
N-alkyl caproanilides (25)
" phthalate - 4 - dicaprylate "
Tri - n - butyl citrate
Triethylene citrate
Diacetate of 2 - nitro - 2 methyl - 1, 3 - propanediol
Dipropionate of 2 - nitro - 2 methyl - 1, 3 - propanediol
Diethylene glycol dipropionate
Triethylene glycol
Hexoxymethyl ether of diethylene glycol
Triethylene glycol di - (2 - ethylhexoate)
Triethylene glycol di - (2 - ethylbutyrate)
β - chloroethyl γ - chloro - γ phenylpropyl ether
Polyethylene glycol 200
Polyethylene glycol 300
Polyethylene glycol 400
Polyethylene glycol 1500
Polyethylene glycol 6000
Polyethylene glycol di - (2 - ethylhexoate)
Dipentaerythritol hexacetate
Dipentaerythritol hexabutyrate
Naphthenic acid - naphthenecyclohexamide
Naphthenic acid - monoethanolamide
Monochlorohydrin glycerol naphthenate
Triethyl phosphate
Tributyl phosphate
Tri xylenyl phosphate
Tri - (2 ethyl hexyl) phosphate
Phenyl bis (β chloroethyl) phosphate
Tris (chloroethyl) phosphate
Tributoxyethyl phosphate
Tricresyl phosphate
Diphenyl mono - (o - chlorophenyl) phosphate
Di - o - xenyl monophenyl phosphate
Tri - (p - tert butyl phenyl) phosphate

Tri - (o - chlorophenyl) phosphate
Tri - (o - xenyl) phosphate
Dimethyl phthalate
Diethyl phthalate
Di - n - propyl phthalate
Di - isopropyl phthalate
Di - isooctyl phthalate
Dibutyl phthalate
Di isobutyl phthalate
Dihexyl phthalate
Dioctyl phthalate
Di - (2 ethyl hexyl) phthalate
Di cyclohexyl phthalate
Di methoxy ethyl phthalate
Di ethoxy ethyl phthalate
Di butoxy ethyl phthalate
Methyl - 2 - methyl - 2 - nitropropyl phthalate
Butyl - 2 - methyl - 2 - nitropropyl phthalate
Bis - (diethylene glycol ethyl ether) phthalate
Silicone oil (Fluid 500)
Diethyl succinate
Di - n - butyl tartrate
Ethyl - p - toluene sulphonate
o - cresyl - p - toluene sulphonate
o and p - toluene ethylsulphonamide
Sulphonated Oil (Naftolen R - 510)
Diphenyl
Diamylnaphthalene
Diamylphenoxyethanol
Benzophenone
Methyl amyldihexylcyclohexanone
Methylcyclohexyl oxalate
Diphenyl sulphone
Triphenylguanidine
Supraflex IX
Flexol P.E.P.

Table 5.

Non degradable plasticisers.

Turning now to point b; the requirements of a biocide for incorporation into a plastic have already been stated. Even if the plastic formulation is itself resistant to biological attack, there might be aesthetic reasons for the incorporation of a biocide so that no microbial growth at all is possible on the surface of the plastic.

In this case microbial spore germination in detritus lying on the surface of a plastic would be prevented by the fungicide or bactericide and microbial overgrowth would be prevented. Compounds commonly used as microbial biocides in plastics can be divided into groups according to their chemical nature.

(a) Organo-Mercury compounds

These compounds have been used frequently in plastics as they are intensly toxic to microorganisms and can withstand temperatures of up to 120°C. Unfortunately they are also toxic to all warm blooded animals including humans, a further disadvantage is that they cannot be used in clear coloured plastics or in sulphur based plastics. Examples of such compounds are Phenylmercuric oleate, Di (phenyl mercury) dodecenyl succinate, phenyl mercuric acetate for use in polyvinyl acetate and acrylics; phenyl mercuric salicylate for polyvinylidene chloride; phenyl mercuric acetate for polyvinyl butyrate; phenylmercuric - o - benzoic sulpimide for cellulosics; phenylmercuric salicylate, phenylmercuric - o - benzoic sulphimide, and phenylmercuric stearate for phenolics.

A solution, dispersion or suspension of HgO in an inert solvent has been quoted for use on polyethylene or polyterprene (presumably as a surface coating) (36). Aryl mercury ammonium salts of halogenated phenols can be used in a variety of plastics (37). Usually these compounds are used at 1 to 2% concentrations and are effective in both thermoplastic and thermosetting resins (38).

(b) Copper compounds

Copper 8 - quinolinolate is frequently used in plastics, it is virtually non volatile (39) and heating has no effect upon its toxic properties. It is frequently used in P.V.C. formulations although it is incompatible with the resin and begins to crystallise or bloom to the surface within a few hours of incorporation. Methods have been developed however to overcome this e.g. Copper 8 - quinolinolate plus the condensation product of toluene - sulphonamide and formaldehyde (40); copper 8 - quinolinolate and an N - alkyl benzenesulphonamide or an N - alkyl toluenesulphonamide (the alkyl group containing 1 to 8 carbon atoms) (41); as in the two above but with cadmium or calcium ricinoleate also present (42); as in (40) the agents being premixed with the plasticiser by heating (43). The above formulations are for use in P.V.C. but (42) and (43) only to be used in P.V.C. when the P.V.C. is not subjected to ultra violet light. Copper 8 - quinolinolate has also been used in polyvinyl butyrate, polyvinyl acetate, phenolformaldehyde, melamine - urea, melamine - ureaformaldehyde. The usual effective concentrations are 1 to 2% but the compound can also be directly (up to 10%) substituted for a susceptible plasticiser (44). Out of 32 biocide preparations tested by Kaplan et al (45) only two, one of which was copper 8 - quinolinolate, were found to provide good protection for treated P.V.C. in direct soil burial and in soil burial following leaching and weatherometer tests.

Copper naphthenate has been found to be ineffective both as a pure compound and in plastics (39) and in P.V.C. coated fabric (46), but Brown (38) reports that this compound, used at 2% concentration in P.V.C. formulations cuts down the amount of fungal growth.

A solution, suspension or dispersion of CuO in an inert solvent can be used as a biocidal coating for polyethylene or polyterprene (36).

(c) Tin compounds

An organotin metal carboxylate (47) at concentrations of 250 to 1000 p.p.m. based on plasticiser content has been found to be a highly effective biocide in P.V.C., polyethylene, polypropylene, polyvinylidene chloride and copolymers thereof.

Bis (tri-n-bulyltin) oxide at 0.03 to 1% has been used in P.V.C. and found to be very stable with no effect upon the properties of the plastic.

Tri-n-propyltin methacrylate in concentrations of up to 10% of the plasticiser content has been used in P.V.C. and found to be effective against Gram positive, Gram negative bacteria and fungi (48).

Bis (tri-n-butyltin) sulphosalicylate is specifically used for flexible P.V.C. at about 0.5% (44).

The organotins are usually 100% active heavy oils, and have an antifungal activity comparable to the mercury compounds but without the high degree of toxicity of mercury. They are not hampered by high concentrations of plasticiser, which tend to neutralise the activity of the mercury compounds.

(d) Sulphur compounds

Zinc dimethyldithiocarbamate in 2% concentrations in vinyl plastics is an effective fungicide (49). The combination of thiocarbamates andmercaptobensthiazoles produces synergistic compositions, the fungicidal properties of which are far superior to those of either of the constituents e.g. Sodium dimethyl dithiocarbamate and the sodium salt of 2 - mercaptobenzthiazole (50); Zinc mercaptobenzthiazole and ferric dimethyl dithiocarbamate (51); ferric salt of mercaptobenzthiazole and zinc dimethyl dithiocarbamate (52); ferric dimethyl dithiocarbamate and bismuth salt of 5 - chloro - 2 - mercaptobenzthiazole (53); and a mixture of zinc dimethyl dithiocarbamate and the zinc salt of mercaptobenzthiazole (54).

A 2 - mercaptobenzthiazole has been used as a bacteriostat in rubbers and plastics (55) whilst other sulphur compounds are given in (56) and (57). Vancide 89 (R. T. Vanderbilt Co. Inc.) at about 1% concentration confers marked resistance to bacterial and fungal attack in vinyl plastics (58).

(e) Substituted phenoxyacetic acids

The ethyl ester of 2 and 4 - methyloxyphenoxy - acetic acid at a 5% concentration has been used to give fungal resistance (59) to certain plasticisers; and 2 - methoxy - 3, 4, 5, 6 - tetrachlorophenoxy - acetic acid, and the dimethyl, diethyl, di - n - propyl, diisopropyl, di - n - butyl esters of 2 - carboxymethoxy - 3, 4, 5, 6 - tetrachlorophenoxyacetic acid were found to give complete protection to P.V.C. at 4 to 5% (60).

(f) Salicylanilides

Brominated salicylanilides are quite stable at the usual processing temperatures and remain biologically active under various environmental conditions. Examples of this class of compound are a 1 : 1 mixture of 4'5 dibromosalicylanilide and 3, 4', 5 tribromosalicylanilide - found to be effective in polyethylene film at 0.1 to 0.3%. However it must not be used for plastics which will come into contact with food stuffs (44).

Zinc salicylanilide has been used as a fungicide for plasticised P.V.C. (61).

(g) Mercaptans

These compounds, particularly N (trichloro - methylthio) phthalimide are widely used in P.V.C. They are claimed to withstand processing temperatures and are non toxic and non irritating to humans at normal usage levels (0.25 to 1%) based on plasticiser weight. This was the other effective compound found by Kaplan (45).

(h) Other Biocides

Hexachlorophene is widely used in polyethylene to maintain a bacterial free surface (62) (63) at concentrations of approximately 1%.

1 - fluoro - 3 bromo (or chloro) dinitrobensene at 0.25% in P.V.C. gave fungal resistance for over six months (64).

Copper and Zinc pentachlorophenoxide has been used in cellulosic plastics and polyethylene at 0.3%.

Pentachlorophenols, particularly Mystox (Catomance Ltd.) have been widely used in P.V.C. formulations and the activity of Mystox is only released in responce to ensymes from microorganisms, thus only coming into use when and where required.

Derivatives of p - chlorometaxylenol are used in P.V.C. and are highly effective fungicides.

3 - alkyl 2, 2' - dihydroxy 3', 5, 5', 6' tetrachlorodiphenyl methane is strongly active against bacteria and fungi in plastics (65).

2, 2' - thiobis - (4, 6 - dichlorophenol); 2, 2' - methylenebis - (3, 4, 6 trichlorophenol), or a mixture of the two can be used to inhibit growth of microorganisms on polyethylene and polyester (66).

A solution, suspension or dispersion of ZnO in an inert solvent can be used as a biocidal coating for polyethylene or polyterprene (36).

A 25% mixture of tri - (2 - chloroethyl) phosphate and not more than 75% dioctyl phthalate plasticiser has been found to produce a fungistatic plasticiser for P.V.C. (67).

Trichlorowthyl phosphate has been used as a fungicide for P.V.C. (68).

Fungicides, in general, can impart a great degree of resistance to microbial attack to a plastic. They are incorporated into a plastic usually in quite small concentrations and are designed to be compatible with the other inclusions in the plastic. Some of the biocides listed above can only be used with certain plastics and only in certain situations, and it is imperative that trade literature be carefully studied and advice sought from manufacturers before deciding upon which biocide to use in which plastic and for what purpose. It seems to be generally agreed that the inclusion of a biocide into a plastic formulation adds very little to the final cost of producing that plastic, and the benefits to be gained from using a biocide far outweigh any monetary considerations.

The facts presented in this chapter from a survey of published literature show that biological breakdown of plastics can be easily prevented by using either resistant polymers, resistant polymers and plasticisers or by the incorporation of selected biocides into the plastics formulation. We must stress, however, that we feel that plastics for use in tropical environments must be rigorously tested on an experimental basis initially, so that the correct combinations of polymer, plasticiser, additives and biocide can be determined in relation to the appropriate environmental conditions.

Chapter 3.

Introduction

The main advantage for using plastics in building materials in the tropics, from a biological point of view, is the obvious resistance to biological attack which can be either an inherent property or a " built-in " property of the plastic. This would lead to an improved life of the building structure itself and would also give greater protection to the contents of such a building by maintaining a more resitant barrier to biological agents. Obvious comparisons here are wood, concrete and metal; needing painted surfaces etc. to prevent decay, penetration, and rusting in the case of metal surfaces. Most plastics can be made self colouring which would obviate the need for painting; here again painted surfaces are particularly susceptible to attack by microorganisms, resulting in flaking and cracking of the paint. Concrete is susceptible to attack by bacteria, fungi and algae, all of which are known to excrete acidic by-products which can slowly wear away the concrete. Surfaces of concrete are not particularly smooth (c.f. plastic surfaces) and form ideal niches for the development of microbial ecosystems. If biological resistance has to be " built into " a plastic by the use of biocides, the biocides are usually more firmly bound into the plastic and are more resistant to leaching than biocides for use in wood.

If we had to think of a possible biological disadvantage for the use of plastics, it could in fact be their resistance to biodegradation when the building structure was no longer needed i.e. it could not be left to " rot away " and finally disappear as do many natural polymeric materials. This however would not really be a problem due to easy scrap disposal of a structural material.

Applications of Plastics in Building

Few plastic products have been in use for as long as the expected lives of the buildings in which they are installed. Predictions of durability, in the light of biodeterioration, must take into account all details of chemical composition, chemical stability, results of accelerated laboratory tests and, most important, the actual behaviour of products that have been exposed to the conditions of use over extended periods, both on weathering sites and in buildings (69).

The main plastics for use in building are listed below, with details of some of their uses in building and their expected behaviour in the light of biodeterioration. Current polymer prices are quoted in Table 6 but should only be taken as a rough guide since within recent weeks major commercial producers have announced increases in the prices of their polymers and all the signs indicate that yet another round of price increases for major chemical products will be required later on. However, it has been pointed out that rapidly rising costs are still not being reflected in appropriate price increases.

Glass reinforced polyesters.

Polyesters weather quite well and show good resistance to biodeterioration. They contain glass fibre and usually additives to improve their fire resistance but the bond between glass fibres and resin is susceptible to attack by moisture and although the process is slow it can lead eventually to structural breakdown (69). These materials can be used for corrugated roof-lighting sheets and the best quality sheets are likely to have a life of 30 years or so. Poor quality sheets may last no more than 10 years (69). They are also used for cladding panels, architectural features, roof trims, window frames, cold water storage tanks. In structural uses it is known that the long term strength of these plastics is considerably less than that measured by short term tests (69). The moisture susceptibility of these materials, combined with the fact that microorganisms live in moist surroundings, must not be overlooked. However it appears that closely controlled manufacture probably holds the key to long term satisfactory performance. Prices for these materials are reasonable (see Table 6).

Phenolic resins

These plastics, usually in the form of resin-bonded laminates have been used as curtain-walling panels, wall linings and corrugated roofing sheets. Their weather resistance is good, particularly if the laminates are heavily impregnated with resin. Resistance to biodeterioration is good depending on the filler or laminating material being used. Microbial growth can be wiped completely off the surface, with no change in properties of the plastic. Their unattractive dark colours may limit their use in tropical regions e.g. they may tend to absorb heat instead of reflecting it and it is known that a 10°C rise in temperature doubles the rate at which chemical reactions leading to polymer breakdown proceed. However the surface of such a plastic could be painted white, but here again a susceptible substrate for microbial attack would be introduced. Prices for this material are reasonable (Table 6).

Amino plastics

Melamine resin-faced laminates have been used for interior working surfaces and wall linings. They do not weather well outdoors and both the polymer and the fillers or laminates are susceptible to biodeterioration.

Urea-formaldehyde resins show good resistance to biodeterioration with no effect upon properties. Prices for both resins are reasonable.

Polyvinyl flouride.

P.V.F. film has recently been introduced for lamination to the surfaces of other materials. Weathering behaviour indicates that, providing the surface is not mechanically damaged, the film is expected to retain its protective and decorative properties for at least twenty years. We have no data on biodeterioration of this plastic but from what has been said above, it would appear to be resistant.

Nylon

Nylon has been used for furniture fittings but its very high price range would probably preclude it from being used in structural applications.

Acrylic resins.

Polymethyl methacrylate has been in use since the second world war for clear and translucent domes, windows, corrugated sheeting etc. The resin itself is resistant to biodeterioration but not the plasticisers. It is subject to damage by scratching although this may not be a serious problem. A life of forty years or more is to be expected. The price of this resin is reasonable.

P.V.C.

(a) Unplasticised (rigid) P.V.C.

This material has been in use for thirty years to date and is mainly used for ventilation ducts, roof lighting and cladding sheets, water mains, drainage, soil and waste systems. Resistance to biodeterioration is good. Roof gutterings are expected to last as long as the buildings on which they are installed, and P.V.C. cold water pipes are now available to British Standard 3505 which ensures a 50 year life under stress. Water above 80°C may cause distortion of P.V.C. drainage pipes. As roof lighting and cladding sheets life expectancy is ten to twenty years, however exposure to high solar temperatures will considerably reduce their expected life.* Resin price is reasonable.

(b) Plasticised (flexible) P.V.C.

This material, in thin film form, is used in building as an alternative to sarking felt, as a metal coating and as waterproof joints between heavy sections of concrete casting. However this material is extremely susceptible to biodeterioration unless resistant plasticisers or biocides are used in its formulation. A very high percentage of all the literature which has been produced to date on the biodeterioration of plastics relates to plasticised P.V.C. The price of this material however is very reasonable.

Polyethylene

Polyethylene as film, sheet or membrane has poor resistance to sunlight and will last only a year or two. The inclusion of 2% carbon black gives a life of ten years or more even when directly exposed to sunlight. Polyethylene shows excellent resistance to biodeterioration. As damp proof membranes and courses it can be expected to last indefinitely. Polyethylene water pipes, with carbon black, should have a life of 50 years (British Standard 1972 and 3284) whilst under continuous water pressure. When used in drains and sinks however polyethylene can be damaged by certain chemical solvents. Cost of this polymer is reasonable.

Polypropylene

Polypropylene has been used in similar situations to polyethylene but in relatively few applications do the advantages held by polypropylene over polyethylene justify its extra cost. It can resist slightly higher temperatures than polyethylene. Its resistance to biodeterioration is good.

Thermoplastics	Approx. cost/metric tonne (1000 Kg)
Acrylic (mldg. powder)	£354
Nylon (different grades)	£615 - £1230
Polystyrene (general purpose)	£138
Polystyrene (high impact)	£166
Polyethylene (L.D.)	£205
Polyethylene (H.D.)	£212
P.V.C. (plasticised)	£197
P.V.C. (unplasticised)	£255
Styrene acrylonitrile	£245
Polypropylene	£235

Thermoset moulding materials	
Phenol formaldehyde (G.P.)	£182
Urea formaldehyde (Std.)	£230
Melamine formaldehyde (GRAN)	£330
Polyester dough moulding compound	£330
Epikote epoxy resins Solid Grade	£640
Liquid Grade	£275

Table 6.

Approximate polymer prices (1970).

The survey of plastics currently in use in the building trade as outlined above would tend to suggest that most of the plastics would give good service in tropical regions (with the exception of plasticised P.V.C. which would be best avoided).

We feel that it would be unwise to recommend certain plasticisers for tropical use until rigorous testing had established their resistance to biodeterioration; the remarks of Elphick (70) that microorganisms have not yet evolved enzyme systems capable of breaking down these man made products, must not be overlooked. Microorganisms are the most adaptive of all organisms.

As we mentioned earlier, the incorporation of a biocide into a plastic confers good degrees of resistance to biological attack on that plastic. Some selected biocides, their representative prices when bought in one hundred kilogram batches and the polymer they can be used to protect are listed in Table 7.

Biocide	Recommended Concentration.	Plastic	Approx. Cost/Kilo
Phenyl mercurics	1 - 2%	Polyvinylidene chloride P.V.A. Acrylics P V Butyrate Cellulosics Phenolics	£3.60
Copper 8 quinolinolate	1 - 2% or up to 10% instead of plasticiser	P.V.C	£4.40
Copper naphthenate	2%	P.V.C.	£0.62½
Zinc naphthenate	N.S.	N.S.	£0.25

Biocide	Recommended Concentration	Plastic	Approx Cost/Kilo
Bis (tri-n-phenylytin) oxide	0.03 - 1%	P.V.C Vinyls	£2.50
Organo-lead compounds	N.S.	N.S.	£2.50
Mercaptans and thiocarbamates	0.25 - 1%	P.V.C Vinyls	£0.50 to £1.00
Substituted phenoxyacetic acid compounds	Up to 5%	P.V.C.	£0.25 to £1.00
Salicylanilides	0.1 - 0.3%	Polyethylene P.V.C.	£1.30
Dichlorophen	N.S.	N.S.	£1.40
Orthophenylphenols	N.S.	N.S.	£0.40 to £0.75
Hexachlorophene	1%	Polyethylene	£1.75 to £2.00
Dinitrobensene componds	0.25%	P.V.C.	£0.50
Pentachlorophenols	0.3%	Polyethylene P.V.C. Cellulosics	£0.20
Pentachlorophenol laurate	N.S.	As above	£0.55 to £0.60
Trichloroethyl phosphate	N.S.	P.V.C.	£0.10 to £0.15

<u>Table 7.</u>

<u>Selected biocides for use in plastics and their approximate prices</u>

These prices are based on the cost of the biocide per kilo if bought in 100 kilo batches.

We consider that there are many uses of plastic building materials in the tropics which would be acceptable to the more intense biological hazards to which they would be subjected in such environments. Indeed, we would consider that in many ways they are superior from a biological viewpoint to many more traditional materials which are presently used in modern building projects in the tropics. However we fully realise that building economics and technology are of paramount importance in deciding whether the use of plastic building materials can be expanded during the present decade. It is clear that biocidal protection may be necessary for such materials and in our tables we have demonstrated that the cost of such protection is very low compared to the cost of the polymeric constituents.

There is no doubt in our minds, and this is borne out by the quoted work in this report, that no plastic building materials should be used in a tropical environment until accelerated tests have been carried out to simulate the possible biological hazards to which the material may be subjected. A list of organisations is appended which have carried out such testing and we strongly suggest that any plastics which are proposed should be so tested. Although we have quoted the probable resistance of plastic components in the body of this report, we have also been at pains to indicate that such reports are often contradictory and results can only be taken as indicative, rather than as definitive. We strongly advise adequate biological hazard testing by an appropriately equipped and experienced organisation before any plastic building material is recommended for use in the tropical environment where a biological hazard is likely.

H. O. W. Eggins ....H O W Eggins........

J. Mills ....John Mills........

19th February, 1971.

APPENDIX.

List of Organisations quoted in " Biological Deterioration Research " 2nd Edition, OEDC 1968.

Austria

Institute for plastics of the Chemical Research Institute of Austrian Industry.

Belgium

Centre Belge d'Etudes des Matieres Plastiques Laboratoires de Chimie et Physico - Chimie

Universite de Liege.

The Netherlands

Central Laboratory TNO

Schoemakerstraat,

P.O.B. 217,

Delft.

Portugal

National Civil Engineering Laboratory,

Avenida do Brasil,

Lisbon.

Switzerland

Ciba S.A.

Research Department - TAP,

Microbiology Laboratory,

Klybeckstrasse,

Basel.

United Kingdom

Commonwealth Mycological Institute,

Ferry Lane,

Kew. Surrey.

<u>United Kingdom</u>

RAFRA,

Shawbury,

Shewsbury,

Shropshire.

<u>United States</u>

Wells Laboratories Inc.

25 - 26, Lewis Avenue,

Jersey City,

New Jersey 07306.

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