

Peroxide Prevulcanisation of Natural Rubber Latex with t-Butyl Hydroperoxide

R.T DAVIES* AND K F GAZELEY*

A peroxide prevulcanisation method involving t-butyl hydroperoxide (tBHP) with fructose as an activator has been studied in detail for its suitability for commercial application. The effects of prevulcanisation temperature, concentration of tBHP, fructose:tBHP ratio and intrinsic iron content on the rate and extent of prevulcanisation have been investigated. Addition of the tBHP in several stages throughout the prevulcanisation, instead of one aliquot at the start, improves the overall crosslinking efficiency. Peroxide prevulcanised latex (PPVL) can be used in conventional coagulant dipping and heat-sensitive dipping processes to produce films with similar unaged properties to those of films made from a low modulus sulphur prevulcanisate. Babies' bottle teats which pass the British Standard requirements for physical properties have been made from PPVL. Unleached PPVL film shows good resistance to heat-ageing but leached film requires an added antioxidant. A mixture of Polygard [tris (mixed mono- and di-nonylphenyl) phosphite] and 2246 [2,2'-methylene-bis-(4-ethyl-6-t-butylphenol)] confers good ageing resistance on PPVL films and does not introduce nitrosamines or nitrosatable amines.

Peroxide prevulcanisation provides an alternative to conventional sulphur prevulcanisation and has the advantage that it does not involve the use of accelerators, some of which can produce carcinogenic nitrosamines¹. Accelerators can also cause allergic skin reactions so peroxide prevulcanisation avoids this problem as well. Methods of peroxide prevulcanisation of NR latex have been studied by Philpott^{2,3}, Gazeley^{4,5} and Ma'zam *et al*^{6,7} and these suggest that the most convenient technique involves adding peroxide to the latex in the presence of fructose (as activator) and a trace amount of iron (which is normally already present in commercial latex concentrate). Ferrous ions react with the peroxide to produce ferric ions and alkoxy radicals. The latter remove hydrogen from the rubber molecules to form rubber radicals which interact to form crosslinks. Fructose reduces the ferric ions back to ferrous ions.

This paper describes recent work in the development of a practical peroxide prevulcanisation system which could be used for

commercial production of latex goods, to study the effect of various reaction parameters on the rate and extent of prevulcanisation, to investigate further the ageing characteristics of peroxide prevulcanised latex (PPVL) films, and to assess the performance of PPVL in coagulant and heat-sensitive dipping processes.

The choice of peroxide is determined partly by its effectiveness but also by its cost, safety and storage stability. Some peroxides and peroxyesters, though effective, have low self-accelerating decomposition temperatures (the lowest temperature at which the compound undergoes runaway decomposition, resulting in a thermal explosion) and are therefore likely to be too dangerous to be favoured for commercial production of PPVL. The peroxide chosen for the present work is tert-butyl hydroperoxide (tBHP). It has a high self-accelerating decomposition temperature ($\geq 80^{\circ}\text{C}$) and good storage stability. It is relatively cheap and reasonably water-soluble so any residual peroxide can, in

*Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford SG13 8NL, United Kingdom

principle, be leached out of the product. The choice of the surfactant used to stabilise the latex during prevulcanisation depends on the application of the latex. In this work an anionic soap, potassium laurate, was used because this surfactant is suitable for use in coagulant-dipping. A non-ionic surfactant may be preferred when the latex is intended for applications using heat-sensitive gelation methods.

It has been observed that leaching results in a loss of tensile strength after ageing in unvulcanised films⁸ and PPVL films⁴ and this is ascribed to the removal of naturally-occurring water-soluble antioxidants. This effect is not significant in sulphur-cured systems due to the protection given by the dithiocarbamate accelerators. The effect of various combinations of leaching and ageing on the physical properties of PPVL cast films was studied.

A major problem with PPVL is its poor resistance to accelerated ageing. Without added antioxidant, a leached PPVL film loses about 80%–90% of its tensile strength on ageing for seven days at 70°C. A leached film made from unvulcanised latex only loses about 10%–20% of its tensile strength under these conditions. It is therefore important to find an antioxidant system which is effective for PPVL. A number of antioxidants were evaluated in cast PPVL films.

A suitable antioxidant should not only give good ageing resistance but must also produce no significant amounts of volatile nitrosamines or nitrosatable amines. Therefore cast films made from PPVL containing selected antioxidants were tested for ageing resistance, and analysed for nitrosamines and nitrosatable amines by the Bundesgesundheitsamt (BGA)⁹ and US Food and Drugs Administration (FDA)¹⁰ methods. For such analyses to be meaningful it is essential that the latex used to make the PPVL is free of the tetramethylthiuram disulphide (TMTD) which is sometimes present in latex concentrate because TMTD decomposes to give zinc dimethyldithiocarbamate (ZDMC) which produces volatile nitrosamines¹¹.

EXPERIMENTAL

Commercial HA latex concentrates were used for all PPVL preparations except where nitrosamine analyses were required. In these cases, a specially prepared HA concentrate known to contain no TMTD was used.

The tBHP was supplied as a 70% aqueous solution by Interlox and the concentration of this solution was checked periodically by iodometric titration. The 20% potassium laurate solution was made up by mixing a solution of potassium hydroxide (BDH) with lauric acid (Unichema International). Fructose was BDH 'Analar' grade. Unless otherwise stated peroxide prevulcanisations were carried out as follows: a 668 g sample of HA latex was poured into a 1-litre beaker, then placed in a water bath at the required temperature and covered with a polythene sheet with a hole in the centre through which a stirrer was passed. The latex was stirred continuously throughout the reaction and aeration was minimised by keeping the stirrer blades below the surface of the mixture and stirring slowly. The peroxide was mixed with 5 g of the 20% potassium laurate solution and about 50 g of water, then added to the latex, followed by the fructose (added as a 20% solution) and sufficient water to dilute the latex solids content to 50%. Small amounts of ammonia were added during the reaction to compensate for evaporation losses. Samples of the latex were taken at regular intervals, chilled rapidly to room temperature, left to dry at room temperature, and used for swelling measurements. Small samples of these dried films were soaked in toluene overnight. The swelling index Q (the ratio of the weight of toluene absorbed to the weight of rubber in the film) was used as an indication of crosslink density.

Iron analyses of latices were carried out by dry-ashing film samples, dissolving the ash in hydrochloric acid and analysing the resulting solution by atomic absorption spectrometry.

Some experiments were carried out as follows to ascertain how much iron is necessary to decompose all of the tBHP in a typical peroxide prevulcanisation mix within a convenient reaction time of 7 h.

A typical PPVL mix (using 0.8 p.p.h.r. of tBHP and a fructose/tBHP mole ratio of 0.6) contains about 267 g of latex serum, 5 g of 20% potassium laurate solution, 20 g of 20% fructose solution, 124 g of water and 5 g of 67.5% tBHP solution. To model the aqueous phase in such a mix, some solutions were made up containing 0.8% tBHP, 1% fructose and 1.8% ammonia. The iron was added as ammonium ferrous sulphate solution. The solutions were stored in stoppered bottles at the required temperature for 7 h (the time by which a typical peroxide prevulcanisation is complete) and then samples were taken for iodometric titration as follows. The test sample (about 1.5 g) was weighed into a small sample tube. The tube and contents were added to 10 ml of chloroform in a 250 ml conical flask under a stream of nitrogen and swirled to mix; 30 ml of 0.0005% of ferric chloride dissolved in glacial acetic acid were added, followed by 5 ml of saturated sodium iodide solution. After the flask was stoppered, swirled and allowed to stand for at least 10 min in the dark, 100 ml of water were added and the mixture was titrated with 0.01N sodium thiosulphate solution to a colourless end-point. The tBHP concentration was calculated using the equation,

$$\text{tBHP concentration (\% w/w)} = \frac{(a-b) \times N \times 8}{w} \times \frac{M}{16} \times 100$$

where a is the sodium thiosulphate titre in millilitres

b is the blank titre

w is the weight of sample (milligramme)

N is the normality of the sodium thiosulphate solution

M is the molecular weight of the peroxide.

The change in concentration of the original tBHP solution added at the start of the experiment was calculated by multiplying by the dilution factor *i.e.* the weight of the whole mixture after the reaction divided by the weight of tBHP solution added at the start. The concentration of the original tBHP solution was found by titration to be 67.5%. The blank

titre, b was found to be zero by doing a titration on a mixture in which tBHP had been replaced by water.

The modulus (M), tensile strength (TS) and elongation at break (EB) of PPVL films were determined according to *ISO 37* except that the dumb-bell test-pieces had extra-wide (25 mm) tabs; wide tabs have been found to give more reproducible test results. The narrow section was 30 mm long and 4 mm wide as specified. Relaxed modulus ($MR 100$) and trouser tear strength were tested according to *BS 1673:4* and *ISO 34* respectively.

Cast films were prepared by pouring latex at 50% total solids content onto a glass plate, drying at room temperature and then leaching and drying if required. All antioxidants were used as standard 40% or 50% dispersions except Polygard which was used as a 33% emulsion stabilised by triethanolamine, oleic acid and casein. The antioxidants were added to the latex after prevulcanisation was complete and before casting or dipping. All cast films were 1 mm thick.

Coagulant-dipped films were prepared on glass plates using 30% calcium nitrate tetrahydrate in methylated spirit, containing 0.3% of Texofor FN30 surfactant (supplied by ABM Chemicals) as a wetting agent. All dipped films were 0.8 mm thick.

The normal leaching method for all films was two 24-h soaks in distilled water at room temperature followed by a 30-min soak in distilled water at 50°C. The film was then dried at 70°C.

Formulations for heat-sensitive dipping were based on the standard mixes given in the *MRPRA Natural Rubber Technical Information Sheet L44*. The dipping tests were done with a glass tube which, because of its low heat retention, was continuously heated to the required temperature by passing water through it from a thermostatted tank. Some babies' bottle teats were made by heat-sensitive dipping and tested according to the *BS 7368:1990* specification.

In addition to the accelerated ageing tests, some samples of cast leached PPVL film

containing various antioxidants were stored in air at room temperature in the dark and the physical properties were monitored over a period of thirteen months.

RESULTS AND DISCUSSION

Prevulcanisation Conditions

Figures 1-5 show the effect of various reaction parameters on the rate and extent of prevulcanisation of an HA latex (which in this case has an iron content of 19.9 p.p.m. on the latex solids). It has been shown^{4,6} that the tensile strength of films made from latex prevulcanised with tBHP reaches a peak at a chemical crosslink concentration around 5×10^{-6} mol/g rubber which corresponds to a Q value in toluene of around 6. While tensile strength is not necessarily the most important requirement in PPVL products (in some cases the modulus is more important), it needs to be fairly high for most applications. Therefore,

the experimental parameters in these tests were chosen so as to concentrate on a fairly small range of Q values around 6.

Figure 1 shows that the final crosslink concentration increases with the initial concentration of hydroperoxide but the initial rate of reaction is not significantly affected. From Figure 2, it is clear that the fructose/tBHP ratio has an effect on the initial rate of prevulcanisation but provided the ratio is above a certain level (between 0.3 and 0.6) it has no effect on the final state of cure. A ratio of 0.3 is too low to give efficient use of the hydroperoxide under these conditions.

In reactions of this kind, there is a risk of producing free radicals faster than they can be utilised in forming crosslinks. There is then a possibility that the radicals will take part in side-reactions resulting in a loss of reaction efficiency. This can be avoided by adding the activator in stages. The effect of adding the

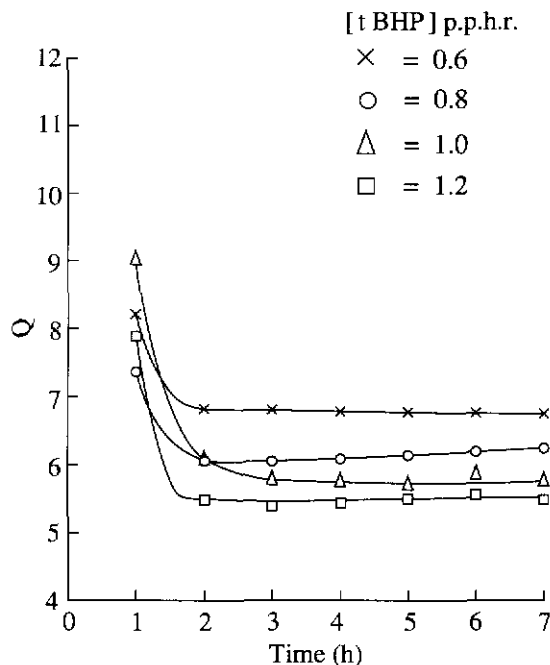


Figure 1. Effect of tBHP concentration on Q . Reaction temperature = 60°C ; fructose/tBHP mole ratio = 1.0

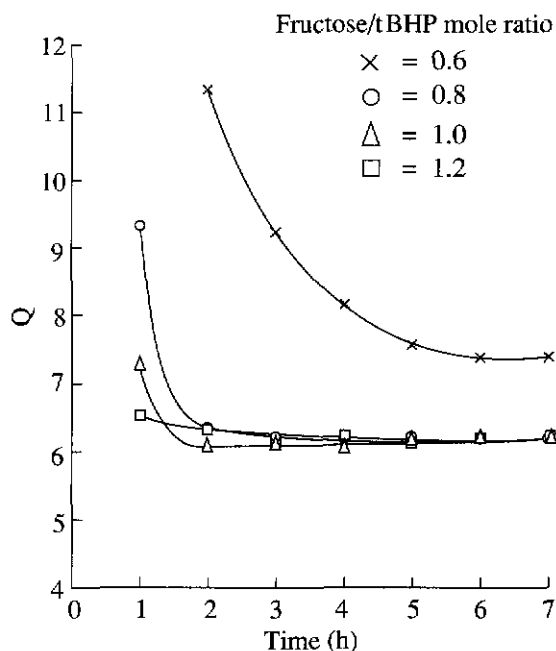


Figure 2. Effect of fructose/tBHP mole ratio on Q . Reaction temperature = 60°C ; tBHP concentration = 0.8 p.p.h.r.

hydroperoxide or the activator in five aliquots during the first 4 h of the reaction is shown in *Figure 3*. Adding the hydroperoxide in stages clearly gives more efficient crosslinking than a normal one-stage prevulcanisation. However, multi-stage addition of the fructose is counter-productive because it reduces crosslinking efficiency.

A comparison of the curves in *Figures 1* and 4 shows that multi-stage addition of hydroperoxide gives more efficient crosslinking over the whole range of hydroperoxide concentrations tested.

The effect of temperature on one-stage prevulcanisations is shown in *Figure 5*. The fructose/tBHP ratio has a more marked effect on the reaction rate at temperatures below 60°C. Clearly, at 40°C, the reaction is too slow to be useful but at 50°C, the reaction can be made to proceed to completion within 5 h by increasing the fructose/tBHP ratio. However, the hydroperoxide is not utilised as efficiently at 50°C as at 60°C.

The iron content of commercial latex concentrate is typically within the range 5-30 p.p.m. on the latex solids, although

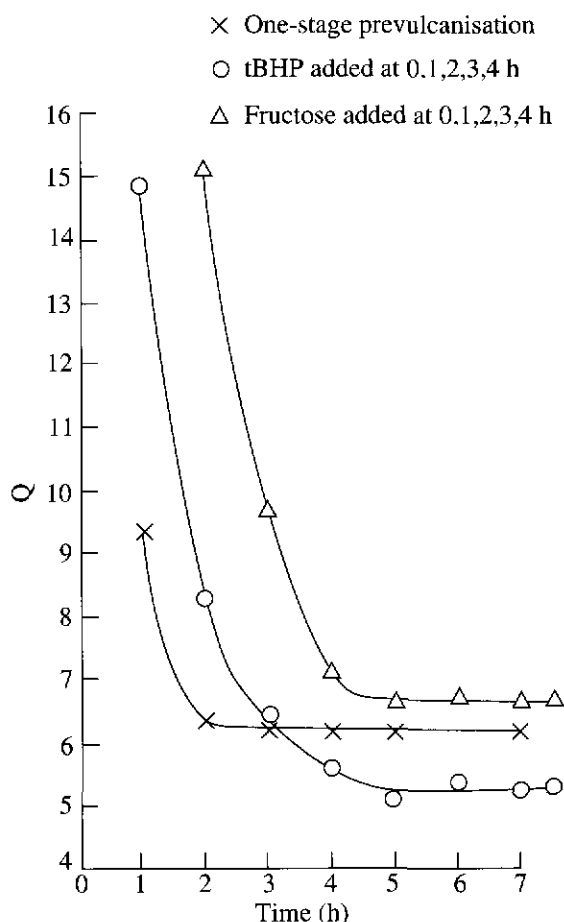


Figure 3. Effect of multi-stage addition of reactants on Q . Reaction temperature = 60°C; tBHP concentration = 0.8 p.p.h.r.; fructose/tBHP mole ratio = 0.6

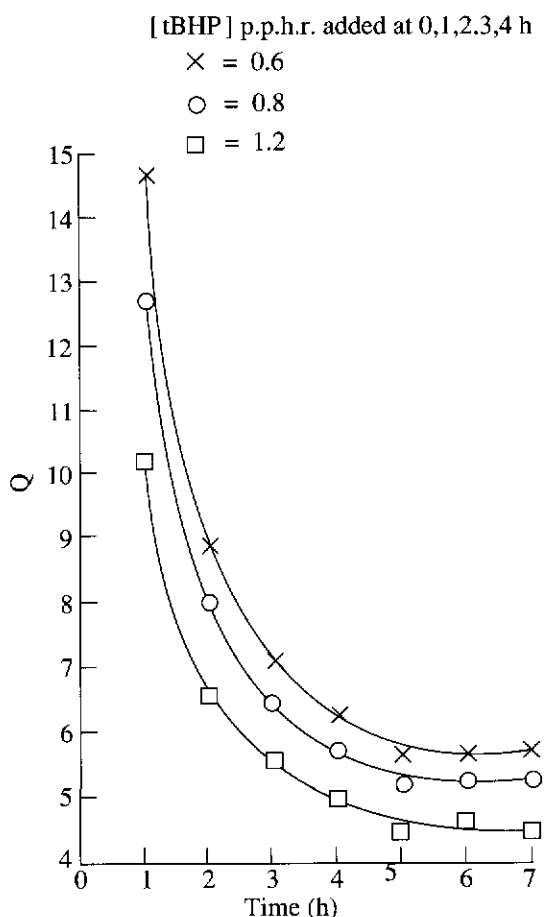


Figure 4. Effect of tBHP concentration on Q for multi-stage prevulcanisations. Reaction temperature = 60°C; fructose/tBHP mole ratio = 1.0

occasionally gross contamination due to a breakdown in the drum or tank lining can lead to higher levels. Free radical processes are known to be sensitive to trace metals and therefore it was necessary to establish the effect of variation in iron content on the peroxide prevulcanisation. Figure 6 shows the effect of iron content on the decomposition of tBHP in a solution which models the aqueous phase in a peroxide prevulcanisation. (No decomposition of tBHP was seen at any of the iron concentrations tested unless both the ammonia and the fructose were present). The results show that at least 2 p.p.m. iron on the latex solids is necessary to ensure decomposition of tBHP within 7 h at 60°C (using a fructose/tBHP mole ratio of 0.6).

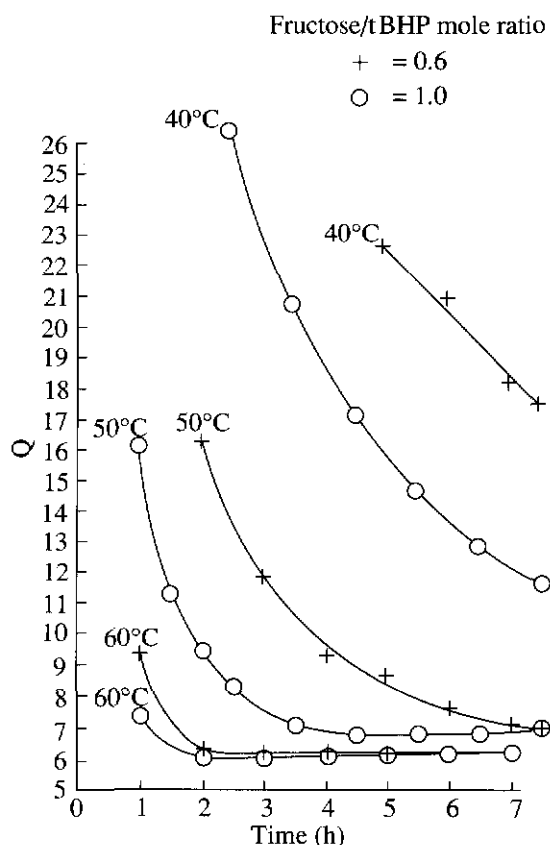


Figure 5. Effect of reaction temperature on Q . tBHP concentration = 0.8 p.p.h.r.

The effect of intrinsic iron content on actual prevulcanisations is shown in Figure 7. It is clear that the prevulcanisation reaction is complete within 7 h even at the unusually low iron content of 2 p.p.m. on the latex solids. At the other extreme, a latex which has suffered gross iron contamination (270 p.p.m.) gives the same rate of prevulcanisation as a latex containing a typical iron content (20 p.p.m.). The final degree of crosslinking increases with iron concentration but this effect should not be very pronounced within the typical range of variation of intrinsic iron content.

Physical Properties of PPVL Products

A collation of physical test results on cast, leached films made from twenty-three PPVLs is shown in Figures 8 and 9. Though the scatter on the results is quite large, the results show the same trends as those reported before^{4,6} except that a narrow peak in tensile strength is seen at a Q value of about 6.8 where tensile strength values of 32 MPa can be attained. This corresponds to a chemical crosslink concentration of about 4×10^{-6} mol/g rubber. Films cast from highly crosslinked PPVL (at a Q value of 4.6) tended to crack during drying.

The physical properties of coagulant-dipped, leached PPVL films are compared with those of a low modulus sulphur prevulcanisate (LR Revultex) in Table 1. The results show that the initial (*i.e.* unaged) physical properties of the two films are very similar.

The results of heat-sensitive dipping tests with PPVL are shown in Table 2. It was found that gelation did not occur in a mix containing

TABLE 1. PHYSICAL PROPERTIES OF COAGULANT-DIPPED, LEACHED FILMS

Property	LR	PPVL
Q	6.1	6.0
Modulus 300% (MPa)	1.1	1.1
Tensile strength (MPa)	30	25
Elongation at break (%)	1100	1000
MR100 (MPa)	0.5	0.5
Trouser tear strength (N/mm)	73	81

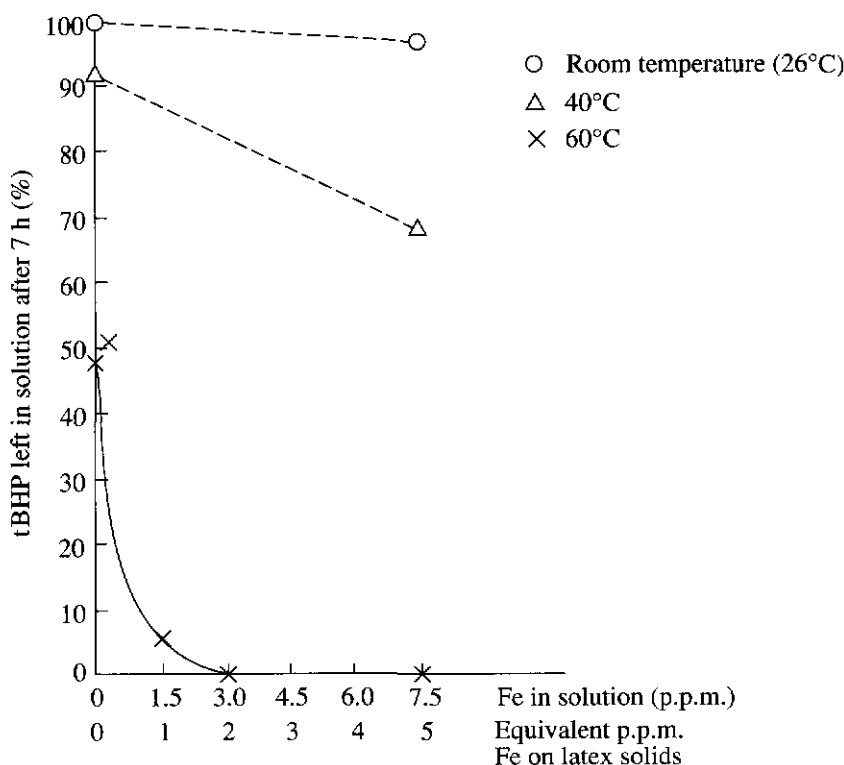


Figure 6. Effect of temperature and iron content on decomposition of tBHP in the presence of 1.8% ammonia and 1% fructose.

the non-ionic surfactant (Texofor FN30) unless zinc oxide was present as an extra gelling agent. This shows that the potassium laurate used as the stabiliser during the prevulcanisation confers some stability on the latex even when the pH has been reduced to 7.9. This is clearly shown by the fact that *Mix 2* which contains no extra stabiliser, gives effective gelation but is also reasonably stable on storage for a week. An equivalent mix made using HA latex instead of PPVL becomes viscous within a few hours. The results in *Table 2* show that a wide range of film thicknesses are available so there are no particular problems in using PPVL for heat-sensitive dipping. A series of babies' bottle teats made from *Mix 2* were found to pass the BS 7368:1990 requirements for surface finish, elasticity, tensile strength and bite resistance.

Ageing Resistance of PPVL Films

Table 3 shows that leaching substantially increases the initial modulus, tensile strength and elongation at break of cast PPVL films. The likely explanation for this is that the leaching process removes hydrophilic material (including residual fructose) which, by retaining water, would tend to weaken the film. This also explains the improvement in physical properties on accelerated ageing because the application of heat would drive off the trapped water. Effects of this kind have been demonstrated previously^{3,4}. It has been shown also that addition of hydrophilic material (a glucose/fructose mixture) to a sulphur prevulcanised latex results in a large loss in tensile strength which can be recovered by leaching¹². The other effect shown in *Table 3* is the large reduction in

TABLE 2 HEAT SENSITIVE MIXES

Compound	Parts by weight	
	Mix 1	Mix 2
PPVL (50% TSC)	200.0	200.0
25% Texofor FN30	2.0	
40% Formaldehyde	To pH 7.9	To pH 7.9
50% Zinc oxide	2.0	
10% Polyvinyl methyl ether (PVME)	10.0	10.0

Immersion time (s)	Former temperature (°C)	Average film thickness (mm)	
		Mix 1	Mix 2
15	40	0.06	0.37
15	50	0.48	1.13
15	60	0.85	1.50
30	40	0.21	0.65
30	50	0.71	1.60
30	60	1.07	2.15
60	40	0.40	1.10
60	50	1.18	2.30
60	60	1.72	2.85

ageing resistance caused by leaching. This suggests that not all of the water-soluble natural antioxidants are consumed during the

prevulcanisation process. Another possibility is that unused fructose, or its reaction by-product, acts as an antioxidant. In Table 4, it is shown that a film which has been aged, then leached, then aged (ALA) is much stronger than a film which has been leached then aged (LA). Therefore the component of PPVL which is responsible for most of the ageing resistance is rendered unleachable by heating for seven days at 70°C. It seems likely that this material is residual fructose, oxidised fructose or some combination of either of these with the natural antioxidants.

Antioxidants

The effect of various antioxidants on ageing resistance is shown in Table 5. All concentrations are expressed as a percentage by weight on the latex solids. A good antioxidant should allow no reduction in physical properties after ageing for at least seven days at 70°C. The results show that Antioxidant 2246 [2,2'-methylene-bis-(4-methyl-6-*t*-butylphenol)] is only moderately effective at the three concentrations tested, as is Irganox 1035 [bis-[beta-(3,5-ditert-butyl-4-hydroxybenzyl)-methylcarboxyethyl]sulphide]. Vulkanox ZMB2 (the zinc salts of 4- and 5-methylmercaptobenzimidazole) is not very effective on its own but behaves synergistically with 2246 to

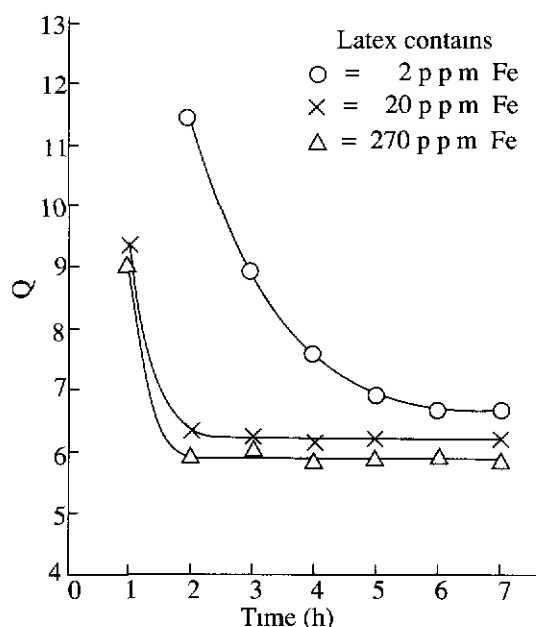


Figure 7 Effect of iron content on prevulcanisation. Reaction temperature = 60°C, tBHP concentration = 0.8 p p h r, fructose/tBHP mole ratio = 0.6

TABLE 3 EFFECT OF LEACHING ON PHYSICAL PROPERTIES OF CAST PPVL FILMS

Property	Cast PPVL film	
	Not leached	Leached
Unaged		
M500 (MPa)	1.11	2.17
TS (MPa)	13.7	23.5
EB (%)	916	1054
Aged 7 days at 70°C		
M500 (MPa)	1.56	1.49
TS (MPa)	27.9	2.17
EB (%)	1076	582
Aged 14 days at 70°C		
M500 (MPa)	1.44	1.42
TS (MPa)	24.2	1.88
EB (%)	1073	577

produce a very effective antioxidant mixture. ZMBT (zinc-2-mercaptobenzothiazole) shows a similar though less marked effect. Thiourea was tested because it is known to decompose cyclic peroxides¹³ (which may be involved in the ageing process in PPVL) and to provide effective protection against metal catalysed oxidation in unvulcanised rubber⁸. However it was found to be almost totally ineffective as an antioxidant for PPVL. The three dithiocarbamates tested: ZDEC (zinc diethyldithiocarbamate), ZBED (zinc dibenzylidithiocarbamate) and Arbestab Z (zinc dinonyldithiocarbamate) are all effective antioxidants. *Tables 6 and 7* show that small amounts (0.2%-0.3%) of ZBED or Arbestab Z are as effective as 1%.

It is important to note that the results in *Tables 5, 6 and 7* were obtained with PPVL made from different HA latices and a comparison of results with 1% ZBED and 1% Arbestab Z shows that antioxidants can be more effective in some latices than others. This effect can also be seen by comparing the results for 1% 2246 and 1% 1035 in *Table 5* with those in *Table 8* of Reference 6. Ma'zam *et al.* found 1035 to be moderately effective and 2246 to be poor, while the present results suggest that 2246 is slightly better than 1035. The reason for these discrepancies is not yet known. Many factors could play a part, for example the freshness of the antioxidant dispersion, the rate of settling of the dispersion during drying of

TABLE 4. EFFECT OF VARIOUS LEACHING AND AGEING COMBINATIONS ON PHYSICAL PROPERTIES OF CAST PPVL FILMS

Treatment	M500 (MPa)	TS (MPa)	EB (%)
—	1.39	16.7	931
L	2.31	24.8	957
A	1.53	24.4	995
LA	1.61	3.45	690
AL	1.75	25.1	998
ALA	1.98	23.7	1011

L = Leached

A = Aged 7 days at 70°C

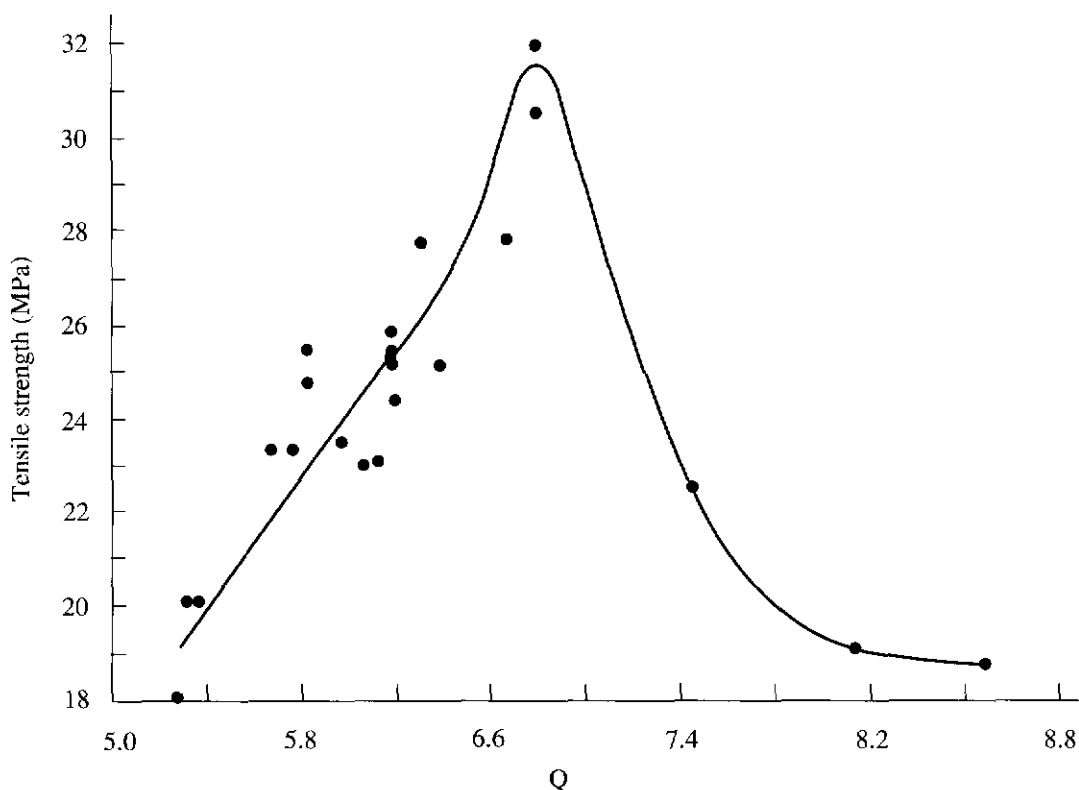


Figure 8. Tensile strength as a function of Q for cast, leached PPVL films

the cast film, the properties of the original latex concentrate or variations resulting from the peroxide prevulcanisation process.

For some applications, defined limits are placed on the nitrosamine content of latex products. For example, the British Standard specifications for babies' bottle teats (BS 7368:1990) and babies' dummies (BS 5239:1988) require less than 30 p.p.b. total volatile nitrosamine content and less than 15 p.p.b. of any one volatile nitrosamine. The volatile nitrosamine and nitrosatable amine contents of cast PPVL films containing ZBED or a ZMB2/2246 mixture are shown in Table 8. The limit of detection is 1 p.p.b. for NDMA and NDEA and 2 p.p.b. for NDBA and NPIP. The control results on PPVL films containing no antioxidant show a very small amount of NDMA in an unleached film. This is reduced by leaching. Very small amounts of

nitrosatable amines are also present. These are expressed as the amounts of nitrosamines produced by acidification of the nitrosatable amines in the presence of sodium nitrite. The nitrosatable amine precursors of NDMA and NDEA are present in very small amounts in both leached and unleached films containing no antioxidant. These amines and the NDMA itself are probably the result of contamination. ZBED and Arbostab Z give no significant increase in volatile nitrosamines or nitrosatable amines. The ZMB2/2246 mixtures are the most effective of the antioxidant systems for PPVL examined here. However, ZMB2 introduces both NDMA and its amine precursor so it is unacceptable for use in teats and dummies.

ZBED and Arbostab Z can be effective antioxidants for PPVL (Table 5) and they do not produce volatile nitrosamines so PPVLs

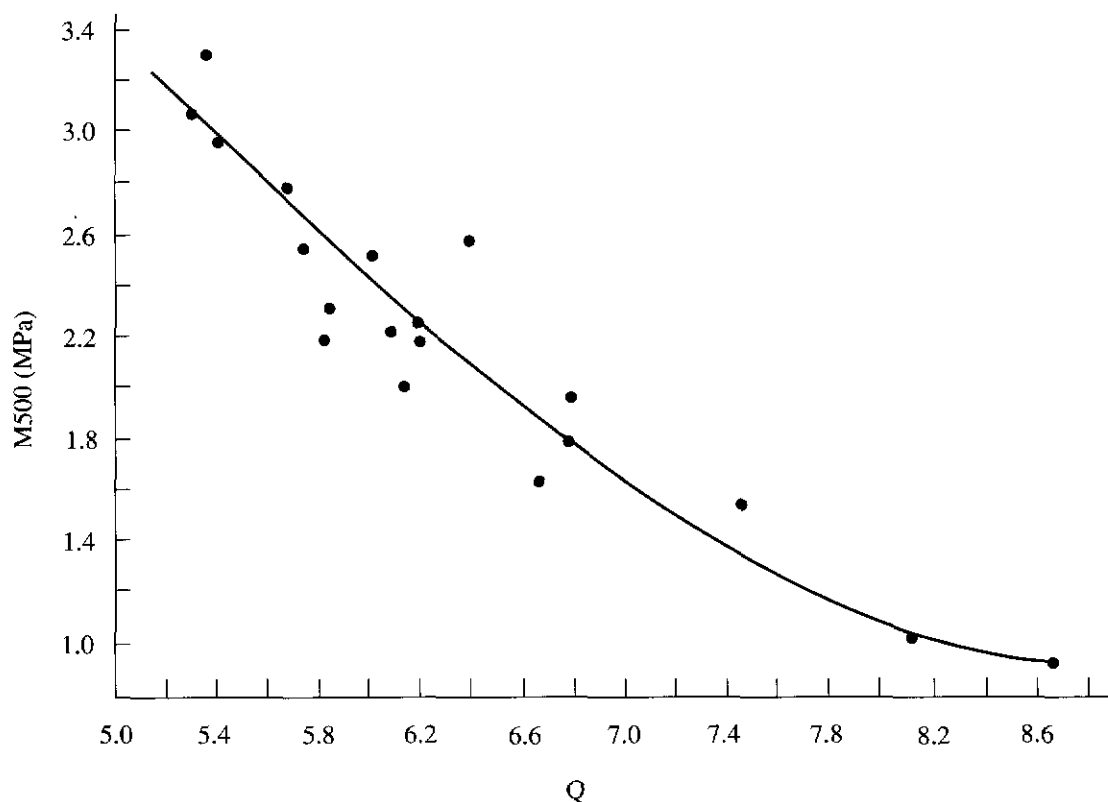


Figure 9. *M500 as a function of Q for cast, leached PPVL films.*

containing these materials will pass the nitrosamine regulations in most countries¹. However it is probable that ZBED (and also Arbostab Z and other long-chain dithiocarbamates) produce non-volatile nitrosamines which are not detectable by the conventional solvent extraction/gas chromatography analysis. The regulations may be extended to prohibit the use of these materials in the future but there is some evidence that the nitrosamine derived from ZBED (nitrosodibenzylamine) is not carcinogenic¹⁴.

The effect of ageing at room temperature for thirteen months is shown in Table 9. The results show that despite the poor resistance of PPVL films to accelerated ageing, long-term storage at room temperature should not be a problem; 0.5% 2246 or ZBED is sufficient to give good ageing resistance at room temperature for thirteen months.

To avoid the nitrosamine problem altogether, it is necessary to use antioxidants which cannot produce nitrosatables at all. Good results have been obtained using a synergistic mixture of Polygard [tri (mixed mono and dinonylphenyl) phosphite] and 2246 (Table 10).

CONCLUSIONS

The efficiency of peroxide prevulcanisation can be improved by multi-stage addition of the peroxide. A threshold level of iron (about 2 p.p.m.) is needed to ensure full decomposition of all the tBHP in a typical peroxide prevulcanisation. The vast majority of commercial latices contain trace amounts of iron which are greater than this. In the unlikely event of a very low iron content the addition of about 20 p.p.m. of iron in solution should solve the problem.

TABLE 5 EFFECT OF VARIOUS ANTIOXIDANTS ON AGEING PROPERTIES OF CAST LEACHED PPVL FILMS

Antioxidant	% retention of property after ageing					
	7 days at 70°C			14 days at 70°C		
	M500	TS	EB	M500	TS	EB
0.5% 2246	89	54	91	N	N	N
1% 2246	92	67	102	N	N	N
2% 2246	85	61	95	N	N	N
1% 1035	79	60	97	N	N	N
2% 1035	85	53	101	N	N	N
1% 2246 + 1% 1035	78	58	94	N	N	N
1% ZMB2	82	57	92	91	44	83
1% ZMB2 + 1% ZBED	89	97	104	97	74	76
1% ZMB2 + 1% 2246	86	107	108	103	100	103
0.8% ZMB2 + 0.8% 2246	106	121	110	96	122	112
0.5% ZMB2 + 0.5% 2246	106	116	110	86	91	105
0.3% ZMB2 + 0.3% 2246	97	89	102	63	42	93
0.3% ZMB2 + 0.8% 2246	107	75	99	63	39	97
0.8% ZMB2 + 0.3% 2246	85	118	111	89	115	109
1% ZMBT	76	22	73	53	15	74
1% ZMBT + 1% 2246	93	88	104	83	65	98
0.5% Thiourea	58	12	68	45	7	60
0.5% Thiourea + 0.5% 2246	72	50	98	63	39	95
1% ZDEC	95	105	103	N	N	N
1% ZBED	94	96	103	N	N	N
1% Arbestab Z	88	97	106	N	N	N

N = Not tested

There is also a threshold ratio of fructose to tBHP below which the efficiency of the reaction drops as well as the rate. Provided this value is equalled or exceeded, the efficiency of the reaction is not increased by further addition of fructose. This threshold value varies with the reaction temperature.

PPVL films of tensile strength greater than 30 MPa can be obtained if the crosslink density is controlled within a fairly narrow range. PPVL can be used in conventional latex processes such as coagulant dipping and heat-sensitive dipping, giving products with physical properties similar to those of a low modulus sulphur prevulcanisate.

TABLE 6 EFFECT OF ZBED CONCENTRATION ON AGEING PROPERTIES OF CAST, LEACHED PPVL FILMS

% ZBED	% retention of properties after ageing					
	7 days at 70°C			14 days at 70°C		
	M500	TS	EB	M500	TS	EB
0	103	19	66	77	10	60
0.2	92	78	81	106	60	88
0.4	101	77	99	95	66	95
0.6	90	76	97	78	67	94
0.8	109	77	95	98	69	93
1.0	107	82	94	100	65	91

TABLE 7 EFFECT OF ARBESTAB Z CONCENTRATION ON AGEING PROPERTIES OF CAST, LEACHED PPVL FILMS

% Arbestab Z	% retention of properties after ageing					
	7 days at 70°C			14 days at 70°C		
	M500	TS	EB	M500	TS	EB
0	85	13	69	77	8	55
0.1	76	73	92	NT	NT	NT
0.3	79	78	103	80	63	100
0.5	72	68	97	68	50	93
0.7	74	66	104	71	47	94
1.0	91	64	96	72	44	94

NT = Not testable

TABLE 8. NITROSAMINE AND NITROSATABLE AMINE CONTENTS IN CAST PPVL FILMS

Treatment	Nitrosamine and nitrosatable amines contents (p.p.b.)					
	FDA Method	BGA Method				
	Nitrosamines	Nitrosamines	Nitrosatable amines			
	NDMA	NDMA	'NDMA'	'NDEA'	'NDBA'	'NPIP'
No leach	ND	1.2	8	9	ND	ND
Leach	ND	ND	4	6	ND	ND
1% ZBED. No leach	ND	1.4	12	14	4	3
1% ZBED. Leach	ND	1.4	8	11	15	2
1% Arbestab Z. No leach	ND	ND	5	1	22	ND
1% Arbestab Z. Leach	ND	ND	2	ND	2	ND
0.8% 2246. No leach	ND	ND	11	2	ND	ND
0.8% ZMB2 + 0.8% 2246	4.0	3.3	218	3	ND	ND
No leach						

NDMA – Nitrosodimethylamine

NDEA – Nitrosodiethylamine

NDBA – Nitrosodibutylamine

NPIP – Nitrosopiperidine

ND – None detected

TABLE 9 EFFECT OF ROOM TEMPERATURE AGEING FOR THIRTEEN MONTHS ON PHYSICAL PROPERTIES OF CAST, LEACHED PPVL FILMS

Antioxidant	% retention of properties		
	M500	TS	EB
–	110	83	98
0.5% 2246	105	106	100
0.5% ZBED	111	106	100
0.5% 2246 + 0.5% ZBED	114	121	103

Leaching of PPVL films improves their initial physical properties but dramatically reduces their resistance to accelerated ageing.

ZBED and Arbestab Z can in some cases give good ageing resistance to PPVL films and do not produce volatile nitrosamines. However

the possible presence of non-volatile nitrosamines means that antioxidants of this type may not be an ideal solution to the ageing problem. Very good ageing resistance is achieved with a mixture of ZMB2 and 2246 but because the ZMB2 seems to be source of

TABLE 10 EFFECT OF POLYGARD AND 2246 ON AGEING PROPERTIES OF CAST, LEACHED PPVL FILMS

Antioxidant	% retention of property after ageing					
	7 days at 70°C			14 days at 70°C		
	M500	TS	EB	M500	TS	EB
1% Polygard	84	25	77	86	28	79
0.5% Polygard + 0.5% 2246	103	125	109	89	84	103
0.8% Polygard + 0.8% 2246	113	128	105	109	119	103
1% Polygard + 1% 2246	89	130	119	94	98	108

volatile nitrosamines and nitrosatable amines, this mixture can only be used in certain applications.

Mixtures of Polygard and 2246 give very good ageing resistance and, because these antioxidants contain no nitrogen atoms, they cannot produce nitrosamines or nitrosatable amines.

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