

Compounding Natural Rubber Latex for Improved Performance

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Undergraded natural rubber as it occurs in latex is characterised by exceptionally high strength and elasticity. Improvements in the performance of latex products are therefore to be sought not so much in enhancing their already excellent elastomeric qualities as in conserving these qualities under increasingly severe conditions. The scope for improving manufactured latex products lies chiefly, though not exclusively, in the direction of increasing their resistance to oxidative deterioration.

Although most manufactured latex products are vulcanised, there are important industrial uses for latex in which the vulcanisation process is omitted. Therefore, the ageing resistance not only of vulcanisates but also of unvulcanised latex deposits is discussed here.

A large proportion, possibly as much as one-third, of the latex currently produced is consumed in areas where the latex plays an adhesive role. For example, reconstituted leathers, fibreboards, bonded hair, non-woven fabrics, tufted carpets and self-sealing envelopes are all composite manufactures in which rubber latex is the binder or sticking component.

Many of the products in which latex is thus employed as a binding medium are not vulcanised. Consequently natural rubber is often the elastomer of choice because, more than most synthetic materials, it combines the qualities of adhesiveness, flexibility and strength in the unvulcanised state.

Provided service conditions are not too severe many of the articles manufactured from unvulcanised natural latex age satisfactorily. This is largely due to the anti-oxidants naturally present in *Hevea* latex. The protective power of the latter can be readily demonstrated by contrasting the ageing behaviour of ordinary NR latex films with that of films deposited from partially purified (multiple creamed) NR latex, or from synthetic polyisoprene latex (Figure 1).

Under severe ageing conditions, or in the presence of deleterious metals, even whole latex rubber (i.e., rubber containing all the non-rubber constituents originally present in the

latex) is liable to degrade rapidly. It is then sometimes necessary or desirable to supplement the natural inhibitors with other protective agents. Selected anti-oxidants of the conventional radical chain-breaking type are often

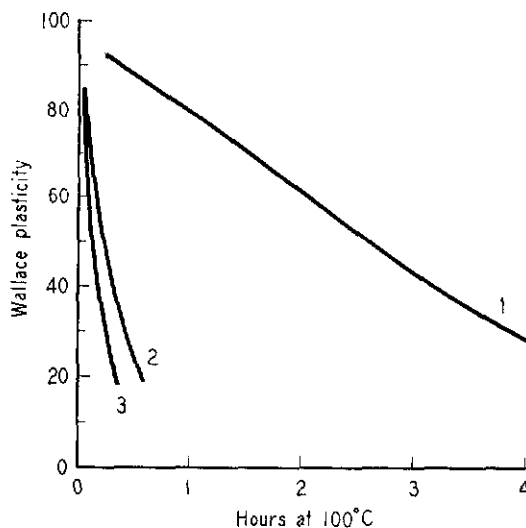


Figure 1. Rate of degradation of latex films in air at 100°C. 1—NR latex; 2—partially purified (four times creamed) NR latex; and 3—synthetic cis-polyisoprene latex.

COMMUNICATION 534

used for this purpose though in fact they are much less effective in unvulcanised than in vulcanised rubber.

Because of the low effectiveness of ordinary anti-oxidants, recent work on the ageing behaviour of unvulcanised latex deposits has been directed towards the manifestly efficient natural protective system. Attempts have been made to identify the active constituents and to reinforce their action by introducing substances of chemically similar type into the latex.

The protective system in *Hevea* contains several, perhaps many, ageing inhibitors. Specifically, anti-oxidant activity is associated with the soluble phosphates (derived from the phospholipins) and with certain amino acids in the latex serum. Furthermore, experiment shows that if ammonium phosphate or a suitable amino compound is added to latex the protective effect of the natural system is augmented.

Among the simple amino compounds which retard the oxidation of unvulcanised latex rubber are various aminophenols (e.g., *m*-aminophenol), amino acids (e.g., glycine), and polyamines. The most effective inhibitors in this class appear to be compounds capable of forming chelate compounds with heavy metals.

Whether phosphates and amino compounds act as true anti-oxidants or as sequestering agents for pro-oxidant metals has not been established; but it may be significant that certain metal sequestering sulphur compounds such as thiourea (PHILPOTT, 1961) also strongly retard the oxidative breakdown of raw natural rubber, both in the presence and absence of catalytically pro-oxidant metals. Three inhibitors—representative of the three compound categories mentioned above—have received particular attention as protectants for unvulcanised latex deposits. They are: (a) diammonium hydrogen orthophosphate $[(\text{NH}_4)_2\text{HPO}_4]$, (b) ethylene diamine tetra-acetic acid (EDTA) (added to latex as the ammonium salt) and (c) thiourea (TU).

The action of these inhibiting agents has been studied in latex by observing the degradation of latex films 1 mm thick after periods of oven-ageing at 100°C. The criterion of degradation

TABLE 1. PLASTICITY OF UNVULCANISED NATURAL RUBBER LATEX FILMS BEFORE AND AFTER OVEN-AGEING—EFFECT OF (A) CONVENTIONAL ANTI-OXIDANTS AND (B) WATER-SOLUBLE INHIBITORS

Inhibitor, p.p.h.r.	Wallace plasticity		
	(i)	(ii)	(iii)
None	83	22	26
Dinonyldiphenylamine 1.0	81	24	35
Di- β -naphthyl p-phenylene diamine 1.0	80	33	38
Diammonium hydrogen phosphate 1.0	81	46	58
EDTA 0.5	85	68	64
Thiourea 0.5	84	70	80

- (i) Unheated
(ii) 4 days at 100°C
(iii) 100 days at 70°C

is the plasticity of the film as measured by the Wallace Rapid Plastimeter.

That the proposed inhibitors retard degradation more effectively than conventional anti-oxidants is evident from Table 1. More striking evidence of their efficiency is given by the data of Figure 2 where various inhibitor combinations have been added to NR latex from which the natural protectants have first been partially removed by multiple creaming. Note that a conventional anti-oxidant [dinonyldiphenylamine (DNDP)] exerts little or no protective effect

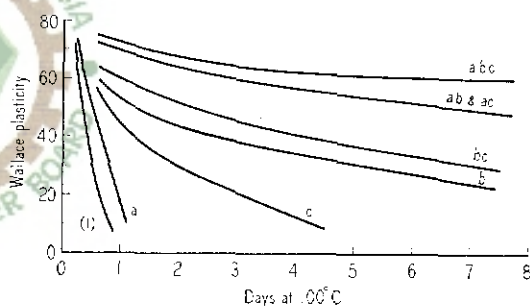


Figure 2. Oxidative degradation of partially purified NR latex films with various inhibitors added singly and in combination. (1)—control (no inhibitor); a—dinonyldiphenylamine (DNDP) 1.0%; b—EDTA/ $(\text{NH}_4)_2\text{HPO}_4$ 0.5/1.0%; and c—thiourea 0.5%.

when used alone but acts synergistically in combination with EDTA or thiourea.

Manufacturers and users of articles containing unvulcanised rubber are sometimes confronted with problems arising from the accelerated degradation of the rubber due to the adventitious presence of copper in the non-rubber component of the article. Traces of copper greatly accelerate the rate at which unvulcanised rubber becomes soft, tacky and ultimately resinous. To counter this type of deleterious action various 'copper inhibitors', for instance di- β -naphthyl p-phenylene diamine, have been proposed; but experience shows that these inhibitors have relatively little beneficial effect on thermal degradation of copper-contaminated natural latex films. More effective protection is conferred by water-soluble inhibitors of the type discussed here, particularly by EDTA and thiourea (*Figure 3*).

For the latex user it is a convenient circumstance that these inhibitors, being readily soluble in water, can be introduced into latex without the aid of emulsifying or dispersing equipment. Despite its solubility thiourea does not appear to be easily extracted from latex films, since films protected with thiourea still age well after being leached in water (*Table 2*).









Inhibitor 0.5 phr	Wallace plasticity after heating at 100°C	
	1 day	2 days
None		
DNPPD		
Thiourea		
EDTA		

Figure 3. Inhibition of copper catalysed degradation of unvulcanised NR latex films.

Copper —100 parts per million

DNPPD—di- β -naphthyl p-phenylene diamine

EDTA —ethylene diamine tetra-acetic acid

VULCANISATION FOR IMPROVED PERFORMANCE

For the majority of latex processes and products a vulcanising system comprising zinc oxide, sulphur and a dithiocarbamate accelerator is entirely acceptable; only in exceptional circumstances it is necessary to depart from this standard type of vulcanising formulation. However, conventional vulcanising systems are not ideally suited to the production of articles that must be (a) exceptionally resistant to heat-ageing, (b) resistant to ageing in the presence of

TABLE 2. PLASTICITY OF UNVULCANISED NR LATEX FILMS WITH AND WITHOUT ADDED COPPER (100 PARTS PER MILLION); OVEN-AGED FOR 2 DAYS AT 100°C —EFFECT OF (A) INHIBITORS, AND (B) LEACHING FILMS WITH WATER

Inhibitor, p.p.h.r.		Wallace plasticity after 2 days at 100°C			
		Without Cu		With Cu	
		unleached	leached	unleached	leached
None		43	17	*	*
Di- β -naphthyl p-phenylene diamine	0.5	58	*	*	*
Diammonium hydrogen phosphate	1.0	69	59	*	*
EDTA	0.5	82	45	81	43
Thiourea	0.5	80	92	86	80

*Too soft to test

copper and other deleterious metals, (c) not susceptible to staining by copper, and (d) resistant to ageing after treatment with organic solvents, *e.g.*, dry-cleaning solvents.

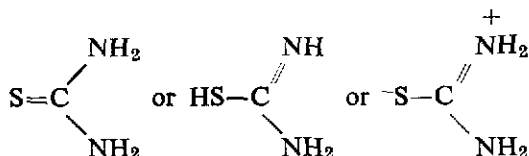
Vulcanisation studies which were originally directed towards (a) — increasing the heat-resistance of latex vulcanisates — have also made it possible indirectly to effect improvements in properties (b), (c) and (d).

Compounding for Heat Resistance

So called 'sulphurless' curing systems in which the sulphur for cross-linking is supplied by an organic sulphur compound [for instance tetramethylthiuram disulphide (TMTD)] have long been used in the compounding of heat-resistant *dry rubbers*. But their application to latex has been limited by their slow rate of action at the relatively low curing temperatures employed in latex technology. The observation that certain substances greatly accelerate the vulcanising activity of thiuram disulphides opened a new route to the formulation of latex rubber with superior resistance to heat and oxidative ageing.

In passing, it may be remarked that vulcanisation with sulphur donors with or without very small amounts of free sulphur is reasonable practice from the stand-point of modern vulcanisation theory. According to current ideas, curing systems with a high ratio of accelerator to sulphur, or with no free sulphur at all, produce vulcanisates in which sulphur is *efficiently* used, *i.e.*, in which the sulphur combined in the network takes the form of short, predominantly monosulphidic cross-links between rubber chains. Such networks are inherently stable, and the resulting vulcanisates age well, have low set and high resistance to reversion.

Among the known activators of TMTD vulcanisation are many sulphur compounds that contain the grouping $\text{HS}-\text{C}=\text{X}$, where X is NH or O. The simplest and most generally suitable of such activators for latex formulations is thiourea (TU), whose structural formula can be written as:



Thiourea is conveniently added to latex as an aqueous solution. Its capacity to activate vulcanisation by TMTD is illustrated by Figure 4 in which Q, the swelling index of the vulcanisate in benzene, is plotted as a function of vulcanisation time at 100°C. Many substituted thioureas, *e.g.*, diphenylthiourea (DPTU), show comparable activating power.

Thiourea-type activation of thiuram disulphides is believed to operate in the following way. The first and rate-controlling step in the vulcanisation of rubber by a thiuram disulphide $\text{RS}-\text{SR}'$ is the scission of the central disulphide bond. At temperatures around or below 100°C, thermal scission of S—S bonds is a slow process and vulcanising efficiency is consequently of a low order. Hence any reagent that facilitates scission should lower the temperature at which vulcanisation proceeds at a relatively fast rate.

Among the extensively studied cleavage reactions of sulphur—sulphur bonds is the nucleophilic attack on S—S by a base Y^- . Subject to steric considerations a displacement reaction of the type:

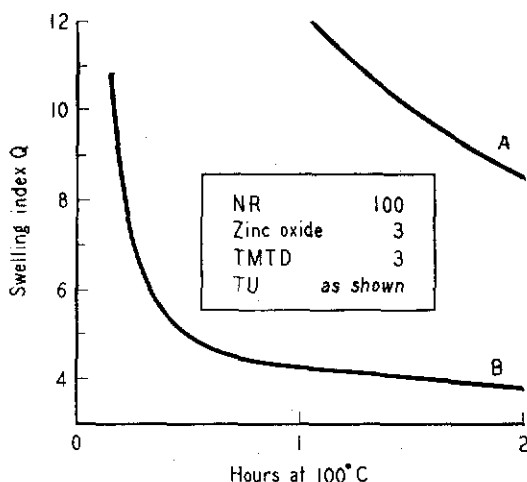


Figure 4. Effect of thiourea (TU) on rate of vulcanisation by TMTD. A—without thiourea; B—with thiourea 1%.

will occur if the attacking base has greater affinity for sulphur than the displaced thio-anion $R'S^-$. Thiourea in its anion form is such a reagent. It activates by virtue of its ability to cleave the thiuram disulphide central bond and liberate the reactive entity $R'S^-$ which is capable of setting off a sequence of fast reactions leading to vulcanisation (PHILPOTT, 1962).

Recent investigations have shown that thio-urea-type activators form efficient curing systems with other sulphur donors besides the thiurams. Indeed sulphur compounds not previously regarded as curing agents for rubber have been shown to be efficient sulphur donors when suitably activated. All these potential curatives are either disulphides $XS-SX$ or sulphenamides $XS-NR_2$ (PHILPOTT, 1965).

The typical sulphur donors shown in *Table 3* are all capable of being activated by thiourea to the extent that they vulcanise rubber, without the aid of elemental sulphur, under comparatively mild conditions. Some of them when used together in pairs act synergistically.

Possibly the most interesting of these curing agents, other than TMTD, is the phosphorus

compound bis (di-isopropylthiophosphoryl) disulphide (DPDS). A useful feature of DPDS is that, unlike TMTD and other thio-carbamyl compounds, it does not form highly coloured complexes with copper. DPDS, preferably in conjunction with a thiazole accelerator, has therefore been suggested as a curative for applications where discolouration by traces of copper must be avoided, for example, in latex thread.

Actual latex compounds formulated with activated curing systems are shown in *Table 4*. The examples illustrate the use of TMTD, MBTS and DPDS as sulphur donors. While some of the recipes shown are strictly sulphurless, others contain a small amount of sulphur. For while it is true that sulphurless systems yield the most stable vulcanisates it is often desirable in practice to include a very small amount of elemental sulphur in order to control more effectively the physical properties (e.g., stiffness) of the vulcanised product. Provided the amount of added sulphur does not exceed about 0.3 per cent resistance to reversion and oxidative degradation is not seriously impaired.


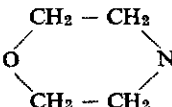
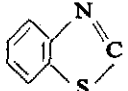
Even without specific protective additives the ageing properties of the resulting vulcanisates are excellent, but in order to exploit the full heat-resisting potential of sulphurless and low sulphur vulcanisates it is usual in technical compounds to include an anti-oxidant. For articles that are expected to encounter high temperatures in service the substituted p-phenylene diamines and ketone-amine condensates are suitable anti-oxidants.

Effect of Copper on Ageing Properties

The behaviour of latex vulcanisates that contain small amounts of copper is of technological importance because many latex products (particularly in the latex/textile field) encounter traces of copper during their service life.

Copper is generally highly injurious to rubber even in concentrations as low as a few part per million. Copper ions are believed to exert their pro-oxidant effect by forming, with hydroperoxides, unstable complexes which readily break down to give chain-initiating free radicals. One method of inhibiting the copper-catalysed

TABLE 3. SULPHUR DONORS CAPABLE OF BEING ACTIVATED BY THIOUREA

Type of sulphur compound	Example	X
$XS-SX$	TMTD	$Me_2NC=S$
"	MBTS	
"	DPDS	$(i-pro)_2P=S$
"	DTM	
$XS-NR_2$	CBS	

TMTD —tetramethylthiuram disulphide

MBTS —di-2-benzthiazyl disulphide

DPDS —bis (di-isopropylthiophosphoryl) disulphide

DTM —morpholine disulphide

CBS —N-cyclohexyl 2-benzthiazyl sulphenamide

TABLE 4. ACTIVATED SULPHURLESS AND LOW-SULPHUR CURING SYSTEMS FOR NR LATEX

Material	Conventional accelerator/sulphur system	'Sulphurless' and 'low sulphur' systems					
		1	2	3	4	5	6
NR as latex	100	100	100	100	100	100	100
Zinc oxide	1	3	3	2	3	2	2
ZDC	1	1	1	3	1	—	—
TMTD	—	3	3	1	—	—	—
DPDS	—	—	—	—	—	3.5	2.5
ZMBT	—	—	1	—	—	0.5	0.5
MBTS	—	—	—	0.5	2.5	0.5	0.5
Sulphur	1	—	—	0.25	—	—	0.3
Anti-oxidant AK	1	1	—	1	1	1	1
Thiourea	—	1	1	0.5	0.6	0.8	0.5
Vulcanisation time	30 to 60 minutes at 100°C						
		Percentage retention of tensile strength after ageing					
Oven-aged 5 days at 100°C	37	74	61	71	74	73	50
„ 10 „ „ „	*	58	42	60	50	54	33
„ 20 „ „ „	*	39	30	34	20	20	15

ZDC —zinc diethyldithiocarbamate

TMTD—tetramethylthiuram disulphide

DPDS —bis (di-isopropylthiophosphoryl) disulphide

*Untestable

ZMBT—zinc salt 2-mercaptobenzthiazole

MBTS—di-2-benzthiazyl disulphide

AK —anti-oxidant of ketone-amine type

reaction is to arrange that the copper ion is sequestered in the form of a stable complex.

In rubber that has been vulcanised with a thiocarbamyl compound any copper that may be present will be converted to its dithiocarbamate. The copper dialkyl or diaryldithiocarbamates are all stable chelate compounds. They not only exert no pro-oxidant activity but are extremely efficient anti-oxidants for rubber. This has been established by both oxygen absorption and stress-relaxation experiments.

It follows that sulphurless vulcanisates which contain high concentrations of thiocarbamyl curatives (TMTD, ZDC, etc.) can accommodate relatively large amounts of copper and still show excellent resistance to oxidative ageing (NATURAL RUBBER PRODUCERS' RESEARCH ASSOCIATION, 1964). In suitably designed rubber vulcanisates, outstanding resistance to reversion and to oxidative breakdown at high temperatures has been achieved by the judicious addition of copper (Table 5).

Under high temperature ageing conditions in which reversion would normally occur copper-containing vulcanisates show remarkably good

modulus retention. This is because in addition to acting as anti-oxidants copper compounds appear to facilitate the formation of new cross-links which compensate to some extent for the degradative effects of oxidation. In this way physical breakdown of the rubber network during ageing and consequent loss of elastic properties is retarded.

In latex compounding it is essential that any copper that is introduced into rubber either deliberately or accidentally should remain in a strongly chelated form during the life of the product; there must be no risk of the copper being released in an oxidative catalytic form. This condition is met in the case of compounds containing large amounts of thiocarbamyl curatives, because mass action tends to keep the copper in the form of a highly stable copper dialkyldithiocarbamate. Another requirement is that the vulcanising system should contain no free sulphur or only a very small amount, e.g., less than 0.2%. As has been mentioned already, the cross-linking efficiencies of vulcanising systems based on thiocarbamyl compounds are increased by traces of copper and unless the

TABLE 5. ACTIVATED SULPHURLESS TMTD VULCANISATES WITH AND WITHOUT ADDED COPPER DIMETHYLDITHIOCARBAMATE 0.2 P.P.H.R. (EQUIVALENT TO APPROXIMATELY 0.04 P.P.H.R. Cu)—PHYSICAL PROPERTIES AFTER PERIODS OF OVEN-AGEING AT 100 AND 150°C

NR as latex	100	100	100	100								
Zinc oxide	3	3	3	3								
ZDC	1	1	1	1								
TMTD	3	3	0.75	0.55								
MBTS	—	—	0.5	0.5								
Cu dimethyldithiocarbamate	—	0.2	—	0.2								
Thiourea	1	1	1	1								
Vulcanisation time, min at 100°C	30	30	30	30								
Physical properties												
Unaged	M	T	E	M	T	E	M	T	E			
Oven-aged 20 days at 100°C	37	330	900	45	330	830	33	350	950	45	380	930
Oven-aged 1 hour at 150°C	13	80	930	48	210	720	*	*	*	59	215	670
" 2 " " " "	21	150	900	51	250	750	21	180	910	54	285	760
" 5 " " " "	16	115	970	43	210	740	11	50	900	45	220	730
" 10 " " " "	10	65	980	34	180	760	*	*	*	33	150	730
" " " " " "	*	*	*	13	65	790	*	*	*	*	*	*

M — Modulus 500% (kg/cm²)T — Tensile strength (kg/cm²)

E — Elongation at break (%)

* Too weak to test

sulphur available for cross-linking is kept at a very low level the ageing vulcanisate develops an excessive number of cross-links (manifested by rising modulus) leading to physical failure by embrittlement.

Generally the most convenient way of introducing copper into a latex compound is to add it as a dispersion of copper dimethyldithiocarbamate or one of its homologues. Alternatively the appropriate amount of cuprammonium chloride may be added to latex before the other ingredients.

Resistance to 'Copper-Staining'

Dithiocarbamate accelerators and other thiocarbamyl curatives, when used in latex compounding, form highly coloured complexes with traces of copper salts. Apart from discolouring rubber, these copper dithiocarbamate complexes are substantive dyes for nylon and other fabrics and trouble can arise from this source in certain latex/textile applications.

The thiophosphoryl analogues of the dithiocarbamate and thiuram curatives do not form strongly coloured complexes with copper and are therefore of interest for the vulcanisation of light coloured latex/textile goods that are liable to encounter traces of copper salts during manufacture or service.

The thiophosphoryl compound bis (di-isopropylthiophosphoryl) disulphide (DPDS) has already been referred to as a copper-non-staining sulphur donor whose vulcanising capacity is potentiated by thiourea. Rubbers vulcanised with DPDS are neither discoloured nor are their ageing qualities adversely affected by copper. If a small amount (*e.g.*, 0.1 p.p.h.r.) of copper dithiocarbamate is introduced into a latex compound containing a fairly high concentration of DPDS the initial brown stain caused by the copper dithiocarbamate is discharged during vulcanisation. The protective properties of copper can thus be exploited in DPDS sulphurless compounds without incurring unwanted staining of the product.

TABLE 6. COPPER-NON-STAINING LATEX COMPOUNDS USING THIOPHOSPHORYL CURATIVES

NR as latex	100	100	100
Zinc oxide	3	3	3
DPDS	3.5	2.5	—
MBTS	0.5	0.5	2
ZMBT	0.5	0.5	—
NaDTP	—	—	1
DNDP	1	1	1
Sulphur	—	0.3	0.3
Thiourea	0.8	0.5	0.5
Vulcanisation time, min at 100°C	30	30	30
Physical properties			
Unaged	M 26	T 325	E 850
Oven-aged 5 days at 100°C	43	240	680
	M 45	T 310	E 750
	140	170	540
	M 34	T 335	E 870
	44	240	720

M—Modulus 500% (kg/cm²)T—Tensile strength (kg/cm²)

E—Elongation at break (%)

DPDS—bis (di-isopropylthiophosphoryl) disulphide

NaDTP—sodium di-isopropyldithiophosphate

DNDP—anti-oxidant dinonyldiphenylamine

An alternative approach to the formulation of copper-non-staining rubbers is to use dibenzothiazyl disulphide (MBTS) as the main sulphur donor in combination with sodium di-isopropyldithiophosphate (NaDTP). Formulations based on DPDS and on NaDTP/MBTS are illustrated in Table 6. At the present time the latter type of curing system may be of greater interest to latex compounders than the former since sodium dialkyldithiophosphates are commercially available whereas DPDS is not.

Resistance to Organic Solvents

Latex rubbers cured with thiocarbamyl compounds—and this includes both conventional and sulphurless TMTD vulcanisates—are highly susceptible to oxidative deterioration after treatment with, for example, dry cleaning solvents. This loss of ageing resistance is due to the extraction by the solvent of anti-oxidants and curative residues which are themselves powerful anti-oxidants. One way of improving solvent resistance is to vulcanise the rubber with curatives that are relatively non-extractable. In general the thiophosphoryl series of

TABLE 7. RESISTANCE OF VULCANISATES TO AGEING AFTER SOLVENT EXTRACTION

NR as latex	100	100	100	100
Zinc oxide	1	3	2	3
ZDC	1	1	—	0.2
TMTD	—	3	—	—
DPDS	—	—	3.5	—
MBTS	—	—	0.5	1.5
ZMBT	—	—	0.5	CBS 1.5
Anti-oxidant	1	1	1	1
Sulphur	1	—	—	—
Thiourea	—	1	0.8	0.8
Vulcanisation time, min at 100°C	30	30	30	30
Tensile strength (kg/cm ²)				
Unaged	320	310	315	315
Oven-aged 5 days at 100°C	120	220	245	240
Oven-aged 5 days at 100°C†	*	*	160	125

*Conventional accelerator/sulphur vulcanisate is untestable after even 1 day at 100°C.

†After extraction for 2 days with cold perchloroethylene

accelerators and sulphur donors appear to be less readily extracted from vulcanisates than the usual thiocarbamyl curatives. Sulphurless vulcanisates containing a mixture of DPDS and MBTS as the source of sulphur show considerable resistance to ageing after solvent extraction (Table 7). Such vulcanisates are not immune to deleterious action by solvents but they remain reasonably resistant to ageing after even prolonged contact with solvents like perchloroethylene; they are also unaffected by washing in water.

Another way of improving the resistance of latex vulcanisates to ageing after solvent extraction is to incorporate 10 per cent of butadiene-acrylonitrile co-polymer (GORTON AND PENDLE, 1965).

A promising new approach to this same problem exploits a recent observation by N.R.P.R.A. that certain anti-oxidants can be so strongly bound into the vulcanised rubber net-

work as to be completely resistant to extraction by organic solvents (CAIN *et al.*, 1969).

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DISCUSSION

Chairman: Dr. J.-P. Poliniere

(Paper presented by Mr. T.D. Pendle)

Mr. H.M. Collier asked if the amount of unvulcanised latex required for carpet-backing justified the production on a field scale of low ammonia latices using either EDTA or thiourea as secondary preservatives; the use of the latter was patented. Mr. Pendle replied that although the potential market in carpet-backing was large, the current consumption of such unvulcanised latex was small. It was too early to predict if there would be widespread acceptance. The recommended formulation used thiourea which was water-soluble and might be added in the field, and a conventional anti-oxidant which probably required emulsification or ball-milling for satisfactory incorporation. Dr. W.L. Resing noted that thiourea corroded metals and asked if any damage to moulds had been observed. Mr. Pendle said no corrosion had been noted and the amount of thiourea in the latex compound was relatively small. Many applications such as foam or plain carpet-backing, threaded or dipped goods, did not involve moulding processes, but the systems described were not recommended for this.

Mr. H.J.M. Langshaw noted that the work reported in the paper was on post-cured latex and asked what results were obtained with pre-vulcanised latex. Mr. Pendle said Mr. Philpott had used pre-vulcanised latex with the thiuram disulphide/thiourea system and the heat resistance was good. The combination of activation by thiourea and pre-vulcanisation with thiuram disulphide was suitable because of the cure temperature below 100°C. Mr. A.D.T. Gorton suggested a system using a low level of sulphur and a high level of ZDC or other accelerator, but Mr. Pendle feared that a high level of dithiocarbamate would increase the copper staining problem. Although there might be advantages in heat ageing, fast cure and high modulus of the vulcanisates with low sulphur/high ZDC systems, these would be more expensive than the high sulphur/low ZDC mixtures.

Mr. S. Kunisawa asked what was the ozone resistance of vulcanisates obtained by the recommended system. Mr. Pendle said exposure of strained samples outdoors indicated that the thiuram disulphide or diethiophosphoryl disulphide systems did not give any better, perhaps slightly worse, resistance to ozone than sulphur-cured vulcanisates. However, this was perhaps unimportant because very few latex articles were either under strain or left exposed to weather.