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An Accelerator System for Transparent Latex Products

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The accelerator combination–TMTD/thiocarbanilide–was tried in NR latex. The transparency of latex films prepared with TMTD/thiocarbanilide combination was found to be superior compared to those films prepared with ZDC/TMTD system. The mechanical properties and ageing resistance of the vulcanisates were compared with those containing ZDC/TMTD accelerator combination. Vulcanisates prepared with TMTD/thiocarbanilide system showed faster curing rate, higher tensile properties and better ageing resistance in comparison to ZDC/TMTD system

The use of organic accelerators is not confined to the increase in the rate of vulcanisation but also in the improvement in physical properties of the vulcanisates[1]. Reduction in vulcanisation time is possible by the use of accelerators. The proportion of sulphur required for optimum physical properties can also be reduced, thus improving the resistance of rubber goods to ageing and preventing blooming of sulphur[2]. The cure characteristics and the mechanical, physical and chemical properties of the product are vastly influenced by accelerators[3]. The heat resistance of the vulcanisate is also determined by the accelerators used and the vulcanisation system as a whole[3]. Accelerators include the thiurams, dithiocarbamates, mercapto-benzothiazoles *etc.* Thiocarbanilide is employed as an accelerator for chloroprene rubber[4]. In the manufacture of high quality products, binary accelerator systems which utilise two or more accelerators in a synergistic manner is of interest[5]. Vulcanisates obtained by using binary accelerator systems are found to have superior physical and chemical properties[5,6]. Mixed in the proper proportions, binary systems can lead to significant improvement in curing behaviour and mechanical properties[7]. Organic accelerators used in latex compounds are basically different from those used in dry rubber compounds[8]. As the vulcanisation temperature for a latex compound is substantially lower than that for the dry rubber compound, the choice of accelerators and their proportion is different from that of a dry rubber compound.

In this study, a new accelerator combination–TMTD/thiocarbanilide was tried in NR latex compound. The percentage transmittance of the sheet was measured by using a UV VIS-NIR spectrophotometer. The mechanical properties of these sheets were also measured. The mechanical properties and percentage transmittance were compared with those containing ZDC/TMTD accelerator combination.

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EXPERIMENTAL

Centrifuged latex (DRC 60%), conforming to *BIS 5430-1981* was used for the study. Other compounding ingredients used namely ZnO, sulphur, TMTD, ZDC, KOH, *etc.* were of commercial grade. Thiocarbanilide was prepared in the laboratory. All water insoluble compounding ingredients were prepared as 50% dispersions, by using a ball mill. The stabilisers used, potassium hydroxide and potassium oleate were prepared as 10% solutions in water.

Thiocarbanilide was prepared in the laboratory by a procedure described elsewhere[9]. A base latex compound was prepared according to the formulation given in *Table 1.*

TABLE 1. FORMULATIONS OF THE LATEX COMPOUNDS

Ingredients	Parts by weight (wet) gm	
60% centrifuged latex	167	167
10% KOH	5	2.5
10% potassium oleate	5	2.0
50% ZnO	1.5	1.0
50% ZDC	2.0	0
50% TMTD	2.0	1.5
50% thiocarbanilide	0	3.0
50% S	1.0	3.0

The centrifuged latex with approximate 0.7 per cent ammonia content was taken in a shallow glass vessel and kept for 3 h–4 h with occasional stirring to reduce the ammonia content to 0.2 per cent. Then all compounding ingredients were added to the latex in the order as shown in *Table 1.* The compounded latex was kept for 24 h for maturation. Latex films were prepared by casting the compounds in glass dishes. After drying the films at room temperature for 24 h, they were vulcanised at 120°C, varying the time from 25 to 40 min in an air oven. Dumbbell shaped tensile pieces were punched out of these cast sheets and tensile properties were measured by using a Zwick universal testing machine. The cure time of the sample for which the maximum tensile strength was obtained, was taken as the optimum cure time.

Spectroscopic Technique for Determining the Transparency

UV VIS NIR spectrophotometer was used to measure the percentage of transmittance of light by each latex film. Very thin films (0.05 mm thickness) of both accelerator combinations were taken and the percentage transmittance was noted at different wavelengths varying from 2500 nm – 250 nm. In order to study the effect of sulphur concentration on transparency, the concentration of sulphur in the latex compound was varied from 0.25 p.h.r. to 2 p.h.r. and the trans-mittance value at a particular wavelength (2000 nm) was determined as there was no change in transmittance with wavelength. ZnO concentration was varied from 0.2 p.h.r. to 1.2 p.h.r. and the percentage transmittance at 2000 nm wavelength was measured.

The amount of clay was varied from 0.5 p.h.r. to 5.0 p.h.r. and the variation in percentage transmittance was also measured. The effect of thickness of the vulcanisate on the percentage transmittance was studied by preparing latex films of thickness varying from 0.025 mm to 0.30 mm. The effect of coagulant on the transmittance of latex films was studied by using a wet coagulant (10% acetic acid) and also a dry coagulant (mixture of calcium nitrate and calcium chloride).

Mechanical properties such as tensile strength, elongation-at-break and modulus of

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cast latex sheets containing optimum quantities of accelerators, cured at optimum cure time were also determined.

Ageing Studies

Test specimens from these sheets were aged in an air oven at 70°C for 3 and 6 days and the retention in tensile strength was determined.

Determination of Volume Fraction (V_r) and Crosslink Density of the Latex Sheets

The vulcanised latex films were subjected to swelling for 48 h in toluene. From the initial weight, swollen weight and de-swollen weight, volume fraction of rubber (V_r) and the crosslink density were calculated.

RESULTS AND DISCUSSION

Figure 1 shows the variation of tensile strength of NR latex vulcanisates of thickness 0.2 mm having ZDC/TMTD and TMTD/thiocarbanilide accelerator systems at different cure times. It shows that for ZDC/TMTD system, as the cure time is increased from 25 min to 40 min, the tensile strength increases, reaches a maximum at 30 min and then decreases. But for the TMTD/thiocarbanilide system, the attainment of maximum tensile strength occurs at 27 min. This shows that TMTD/thiocarbanilide is a faster accelerator combination compared to ZDC/TMTD system. The tensile strength of sheets with TMTD/thiocarbanilide system is higher than those of ZDC/TMTD system. This may be due to the more homogeneous distribution of water soluble thiocarbanilide in the latex compound.

Figure 2 shows the percentage transmittance of ZDC/TMTD and TMTD/thiocarbanilide systems at different wave-lengths (2500 nm to 250 nm). As the wavelength decreases, for the ZDC/TMTD system, there is a gradual decrease in the percentage transmittance whereas for the TMTD/thiocarbanilide system, the same percentage transmittance is maintained over the entire region of wavelength.

From the figures it is clear that almost 80% of the light is transmitted by latex sheets of TMTD/thiocarbanilide system whereas for sheets with ZDC/TMTD system, the percentage transmittance is much lower. This proves that films of TMTD/thiocarbanilide are more transparent. This superior transparency also may be due to the homogeneous dispersion of thiocarbanilide in the latex compound. NR latex is preserved with ammonia and even at the time of compounding, latex contains approximately 0.2% ammonia which facilitates the dissolution of thiocarbanilide in NR latex.

Figure 3 shows that as the concentration of sulphur increases in the latex compound, the percentage transmittance decreases. When the sulphur concentration is high it may result in the formation of crystals of free sulphur in the matrix and eventually sulphur blooming may reduce the transmittance.

Figure 4 shows that as the amount of ZnO in the latex compound increases, the film becomes less and less transparent. The high tinting power of zinc oxide may be the reason for significant reduction in transparency.

Figure 5 shows the effect of a filler (clay) on the transparency of the latex film. As the amount of clay increases in the compound, the transparency decreases. This reduction in transparency may be caused by the scattering of light by the rubber particles. When there is a large difference between the refractive index of rubber particle and filler, this above effect will be found.

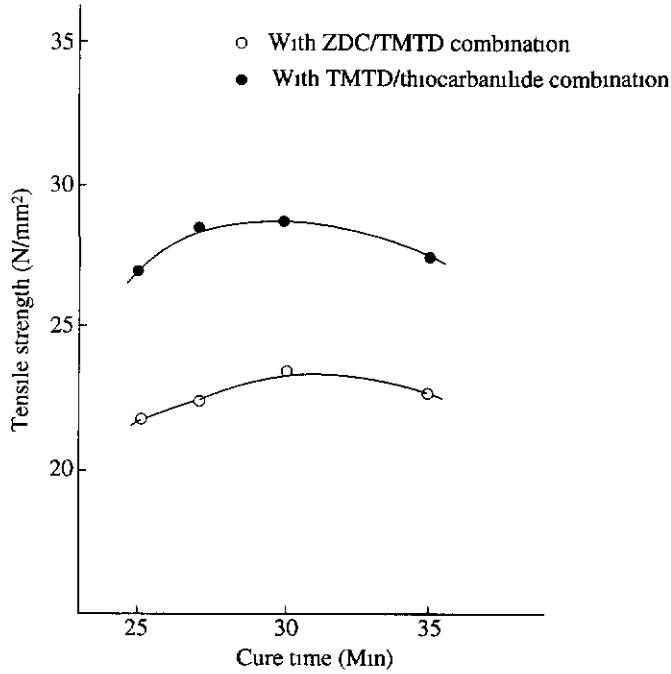

Figure 1 Variation of tensile strength of latex vulcanisates with increase in cure time

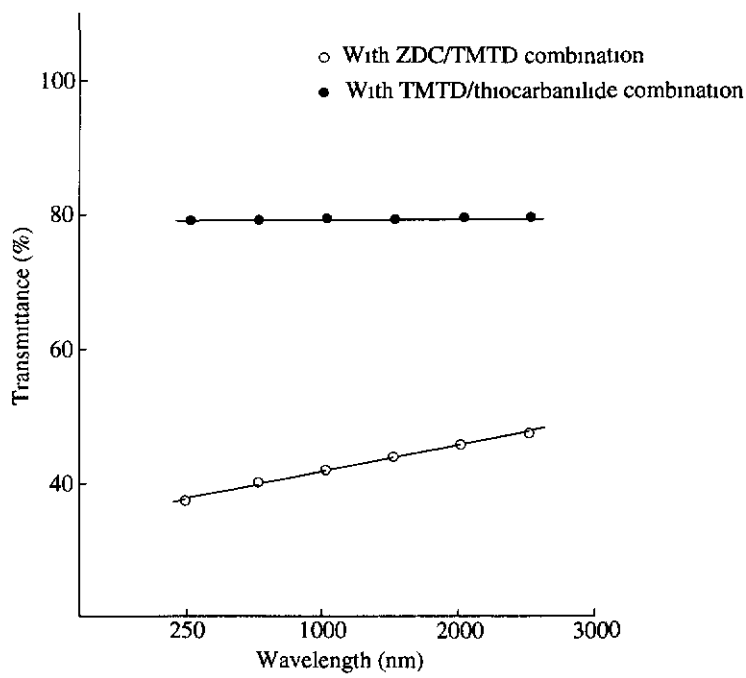

Figure 2 Percentage transmittance of latex vulcanisates of thickness 0 05 mm at different wavelengths

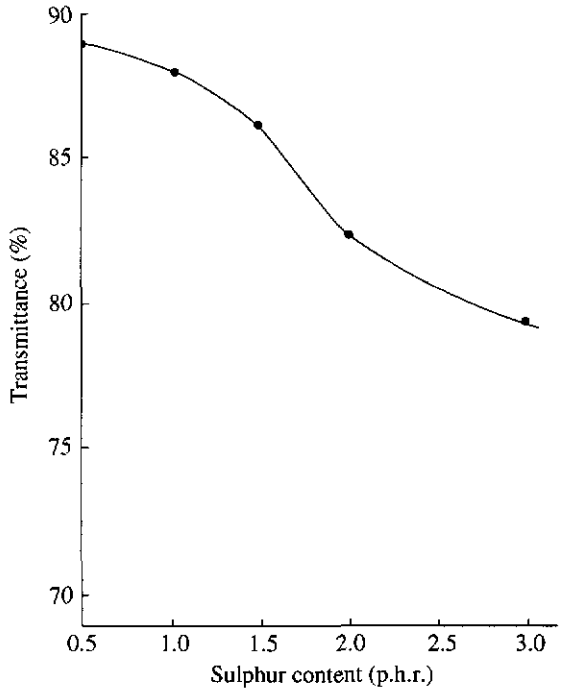

Figure 3 Variation of the percentage transmittance with concentration of sulphur (thickness kept constant).

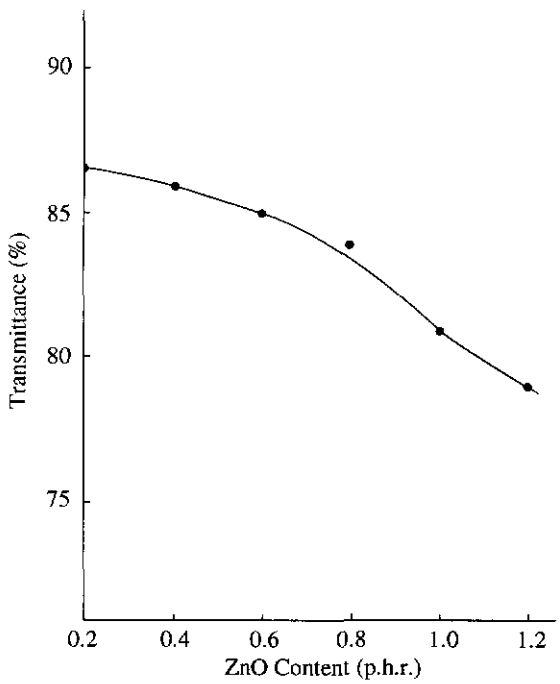

Figure 4. Variation of the percentage transmittance with ZnO content (thickness kept constant).

Figure 6 shows the relationship between thickness of the latex film and its transparent nature. It is shown that transparency is inversely proportional to thickness of the film. Optical density (absorbance) is generally proportional to thickness, therefore transmittance must decrease with increase in thickness.

Table 2 gives the variation in tensile strength of the latex vulcanisates after ageing. Here also, the ageing resistance is found to be superior for TMTD/thiocarbanilide system. The enhancement in tensile properties and ageing resistance may be attributed to improved dispersion of the thiocarbanilide in NR latex.

Table 3 shows the variation of elongation at break, modulus and tear strength of latex sheets with TMTD/thiocarbanilide and ZDC/TMTD systems. For ZDC/TMTD system the elongation-at-break is slightly higher which may be due to the lower crosslink density. The modulus of sheets with TMTD/thiocarbanilide system is slightly higher. TMTD/thiocarbanilide system has a higher tear strength. The improved tear strength may be due to the uniform crosslinking in the vulcanisate.

Table 4 shows the V_r values and crosslink densities of latex vulcanisates with ZDC/TMTD and TMTD/thiocarbanilide systems. The crosslink density is somewhat higher for the TMTD/thiocarbanilide-cured rubber. This is in accord with the values of the somewhat increased modulus and reduced ultimate elongation. Also, the tear strength is somewhat improved in the case of the TMTD/thiocarbanilide-cured rubber.

TABLE 2. VARIATION OF TENSILE STRENGTH OF LATEX VULCANISATES AFTER AGEING

Accelerator system	Tensile strength (N/mm^2)		
	Original	Aged at 70°C after 3 days	Aged at 70°C after 6 days
TMTD/Thiocarbanilide	29.0	27.0	25.2
ZDC/TMTD	23.5	21.0	18.5

TABLE 3. VARIATION OF ELONGATION-AT-BREAK, MODULUS AND TEAR STRENGTH OF LATEX VULCANISATES

Accelerator system	Elongation-at-break (%)	Modulus (100%) (N/mm^2)	Tear strength (N/mm)
TMTD/Thiocarbanilide	665	0.83	56
ZDC/TMTD	840	0.78	44

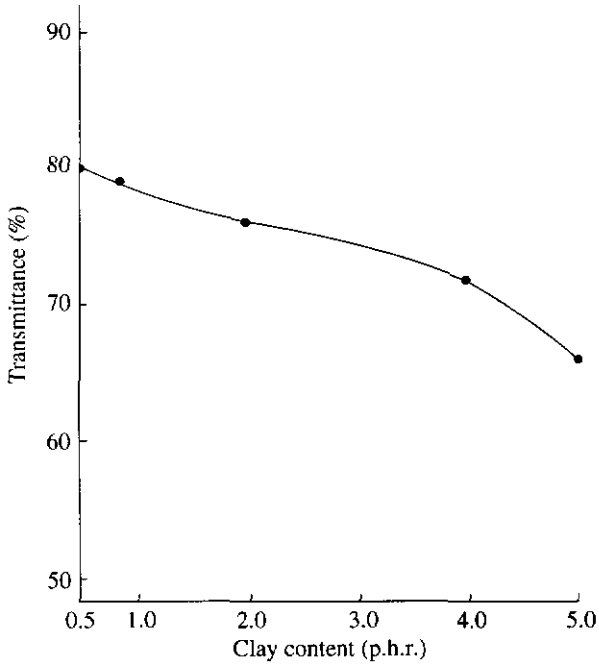

Figure 5. Variation of the percentage transmittance with filler content (thickness kept constant).

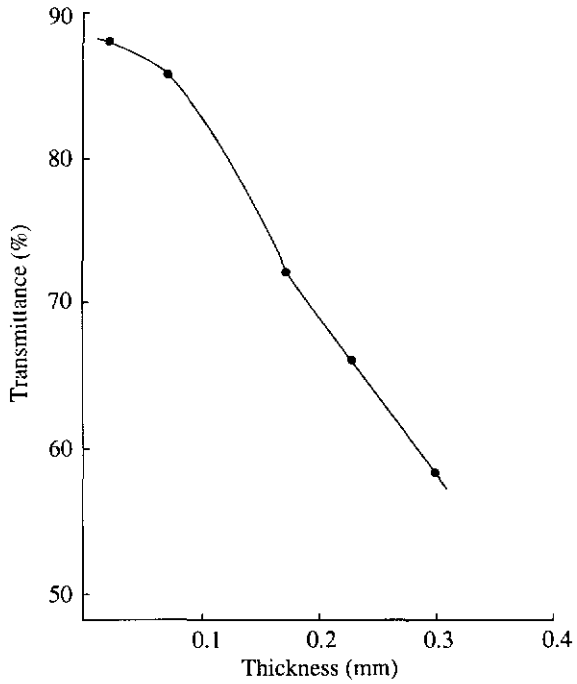

Figure 6. Variation of the percentage transmittance with thickness of the latex film.

TABLE 4. V_r VALUES AND CROSSLINK DENSITIES OF LATEX VULCANISATES

Accelerator system	V_r value	Crosslink density (gm mol/cc)
TMTD/Thiocarbanilide	0.182	4.5×10^{-5}
ZDC/TMTD	0.172	3.99×10^{-5}

CONCLUSION

TMTD/thiocarbanilide system is found to be a fast curing accelerator system. This system gives latex sheets of enhanced tensile strength and ageing resistance. Their transparency is superior to those of films prepared with ZDC/ TMTD accelerator system. Therefore this new accelerator system has potential in natural rubber latex systems, particularly for making transparent products.

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