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FACTORS AFFECTING TRANSPARENCY OF NATURAL RUBBER LATEX FILMS

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The different factors affecting transparency of films made from natural rubber latex have been investigated. The effect of sulphur, zinc oxide, oil, antioxidant, fillers, viscosity modifiers, coagulants, type of latex and humidity were studied. As sulphur dosage is increased, transparency of NR latex film increases, reaches a maximum and then decreases. The presence of zinc oxide in the film decreases transparency. The particle size of zinc oxide affects transparency of the film. Paraffinic oil and styrenated phenol type antioxidant do not affect transparency of the films. Fillers decrease transparency considerably. Centrifuged latex and creamed latex give comparable transparency to the film. Clarification of prevulcanized latex and heat treatment of the film substantially improve transparency especially when clarification is done by centrifuging. Exposure of the films to a humid atmosphere decrease transparency. Films made by straight dipping are more transparent than those made by coagulant dipping.

Key words – Natural rubber, Compounding ingredients, Prevulcanized latex, Coagulants, Fillers, Viscosity modifiers, Antioxidants.

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INTRODUCTION

Latex mixes, which yield transparent films on drying, are often preferred for products like rubber band, certain types of gloves, tubing, teats and soothers although transparency is not an important technological property for rubber products. Production of transparent rubber articles requires special attention in the choice and proportion of compounding ingredients. Fillers for transparent products should have an index of refraction very close to that of rubber as otherwise the filler particles may cause opacity to the finished product. Sulphur, accelerators, activators, etc. used in latex compounding also have marked influence on the transparency of the product.

Studies on transparency of vulcanizates from dry rubber have been reported (Johnson and Scott, 1943; Wolf, 1957; Wolf and Stueber, 1960; Mani *et al.*, 1980). The effect of formulation on the dry film transparency of prevulcanized latex has been reported by Gorton (1979). Latex films prepared using the activator/accelerator complex FIC 3/5, are reported to have higher transparency than those obtained using zinc oxide (Gorton, 1988).

In the present work various factors affecting transparency of films made from NR latex have been investigated with a view to designing formulations and developing manufacturing techniques which will render maximum transparency.

MATERIALS AND METHODS

Centrifuged latex conforming to the specifications of the Bureau of Indian Standards (BIS), IS:5430–1981, and field latex from the RRII Experiment Station were used for this study. The other compounding ingredients were of commercial grade. Vulcanizing agents and fillers were used as 50 per cent dispersions in water. Antioxidant and process oil were used as 50 per cent emulsions in water. Surface active agents were prepared as 5 per cent solutions in water.

The base formulation selected for the study is given in Table 1. The compound was matured for 24 h and films were prepared by casting the compound in shallow glass dishes. The films were dried for 48 h at 30°C and vulcanized at 100°C in air for one hour. The films were designated as 'post vulcanized films'. Specimens, 5 x 1 cm size, were cut and fixed on a glass plate of the same size by means of two small strips of adhesive tape at both ends. The transparency of the film was measured using a Shimadzu UV-Visible Recording Spectrophotometer (UV-240) which gives values for light transmission at wavelengths ranging from 300 to 900 nm. The transmittance values at a wavelength of 600 nm, at which maximum light transmission was obtained, were recorded. Absorbance of the supporting glass plate was adjusted to zero in all measurements.

Table 1. **Formulation of the base compound**

Ingredients	Parts by weight (wet)
60% Centrifuged latex (HA type)	167.0
10% Potassium hydroxide solution	2.5
50% Sulphur dispersion	4.0
50% Zinc diethyldithiocarbamate dispersion	2.0
50% Zinc oxide dispersion	0.4

Latex films of thickness, ranging from 0.2 to 1 mm, were prepared using the base compound to study the effect of film thickness on transparency. In all the other experiments the thickness of the film was adjusted to 0.5 mm. The period of heating ranged from 0 to 3 h. This treatment is inclusive of the time required for vulcanization in the case of post vulcanized films. The sulphur concentrations studied were 0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 parts per hundred rubber (phr). Six different batches of the compound were made using 50 per cent zinc oxide dispersions prepared by ball milling for different periods of time. Ball milling was done for 0, 6, 12, 18, 24 and 48 h. To study the effect of concentrations of zinc oxide, the dosages tried were 0, 0.1, 0.2, 0.3, 0.4 and 0.5 phr. Styrenated phenol based antioxidant was added as a 50 per cent emulsion to the base formulation at the levels of 0, 0.5, 0.75, 1.0, 1.25 and 1.5 phr to ascertain the influence of antioxidant concentration. Paraffinic oil, at 0, 1, 2, 3 and 5 phr, was tried as a 50 per cent emulsion to the base formulation. Surface active agents employed were polyvinyl alcohol, ammonium alginate, carboxymethyl cellulose and casein and the concentrations were 0, 0.25, 0.5, 0.75 and 1.0 phr. The fillers studied were precipitated silica, whiting, magnesium carbonate, china clay and titanium dioxide.

Field latex and creamed latex, in addition to centrifuged latex, were studied. The latex compound was prevulcanized by heating at 70°C for 2 h. A portion of the prevulcanized latex was centrifuged at 3000 RPM for 10 min and then decanted out. In another portion of prevulcanized latex, instead of centrifuging, excess solid ingredients were allowed to sediment by keeping the latex undisturbed for different periods. Prevulcanized latex films were kept at different levels of humidity for 48 h before measuring transparency. Instead of casting, latex films from the base compound were prepared by coagulant dipping to study the effect of coagulants. Five per cent solutions of formic acid, acetic acid and calcium nitrate were used.

As per the selected formulation (Table 3) post vulcanized and prevulcanized latex films were prepared. Physical properties of these films were evaluated in comparison with those of films from a conventional formulation used for preparing rubber band.

RESULTS AND DISCUSSION

Figure 1 shows the effect of thickness of latex film on transparency. It is seen that as the thickness of the film increased transparency has decreased. This is expected, as rubber vulcanizates can never be fully transparent. As the thickness of a less transparent material increases light transmittance is bound to decrease. In all the other experiments the thickness of the latex film was maintained at 0.5 mm. The effect of heating of latex films on transparency, as shown in Fig. 2, shows that heating increases transparency of latex films and the maximum transparency is obtained

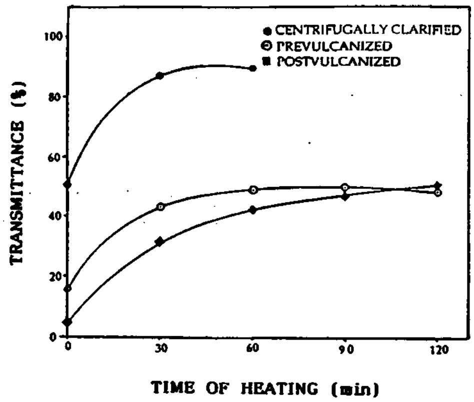

Fig. 2. Effect of heating of latex film on transparency

at a heating time of 1 h and thereafter the increase is not appreciable. Before heating, the latex films contain compounding ingredients like sulphur, in the free state. During the course of heating, a major portion of these ingredients get used up in reactions with rubber, which improves transparency. Heating of the film also removes the final traces of moisture present in the film, further improving transparency. In all the other experiments the time of heating of the latex films was fixed as 1 h.

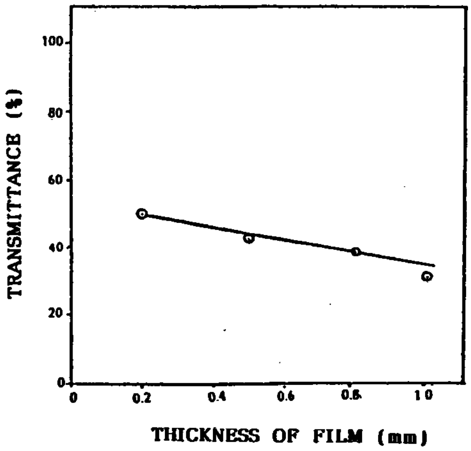

Fig. 1. Effect of thickness of latex film on transparency

The effect of adding sulphur on transparency is shown in Fig. 3. As the dosage of sulphur increased, transparency increased initially and the maximum transparency was obtained at a sulphur dosage of 1 phr. On further increasing the level of sulphur, a decrease in transparency was observed. Therefore, for obtaining maximum transparency, sulphur level should be maintained at 1 phr. It may be mentioned that when sulphur dosage is increased beyond the optimum level, the quantity of free sulphur remaining in the vulcanized film increases resulting in the formation of crystals of free sulphur in the matrix and eventually in surface blooming.

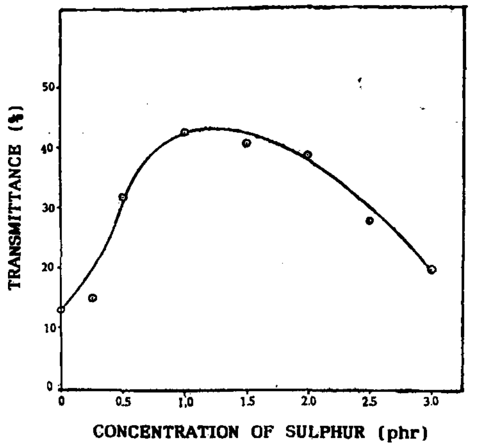

Fig. 3. Effect of concentration of sulphur on transparency

Insoluble solid ingredients are added to latex as fine dispersions which are prepared by ball milling. This process reduces the particle size of the ingredients. To find out the effect of degree of ball milling on transparency, 50 per cent zinc oxide dispersions, prepared by ball milling for different periods of time, were added to the base compound and the transparency of the films, prepared therefrom, determined. The results (Fig. 4) show that as the ball milling period is increased transparency also increased upto a period of 24 h and thereafter the change was not appreciable. This shows that transparency of latex vulcanizates is affected by the particle size of the solid ingredients and as the particle size is reduced transparency is increased. A ball milling period of 24 h reduces the particle size of zinc oxide to the optimum level for the purpose of transparency.

The effect of adding different amounts of zinc oxide on transparency (Fig. 5) reveals that the addition of even small amounts of zinc oxide into the latex compound decreases transparency of the films considerably. The high tinting power of zinc oxide is responsible for the significant reduction in transparency. For obtaining maximum transparency, it is advisable to avoid zinc oxide.

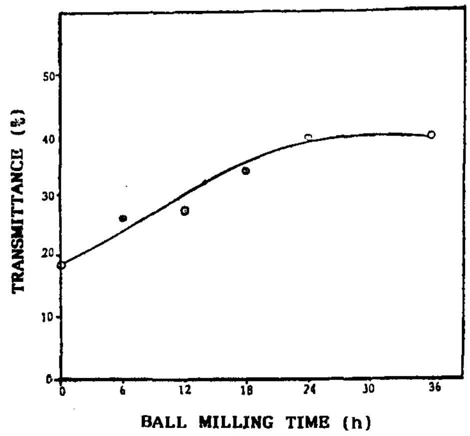

Fig. 4. Effect of ball milling time of zinc oxide on transparency

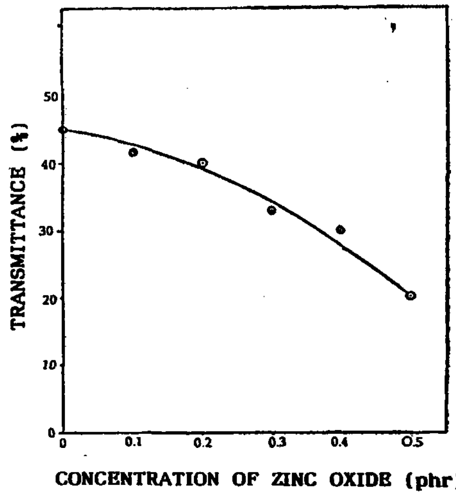

Fig. 5. Effect of concentration of zinc oxide on transparency

For special applications, process oils are added to latex during compounding. It is seen from Fig. 6 that transparency of the latex films remains largely unaffected by the addition of paraffinic oil upto the level of 5 phr.

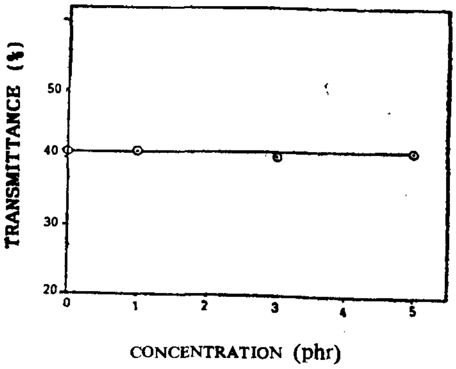

Fig. 6. Effect of concentration of paraffinic oil on transparency

For preparing a good quality rubber product, antioxidants are usually added during compounding which protect the products from deterioration by oxygen, ozone, heat, light etc. The results as depicted in Fig. 7, show that transparency of the latex film is not significantly affected by the presence of styrenated phenol type antioxidant.

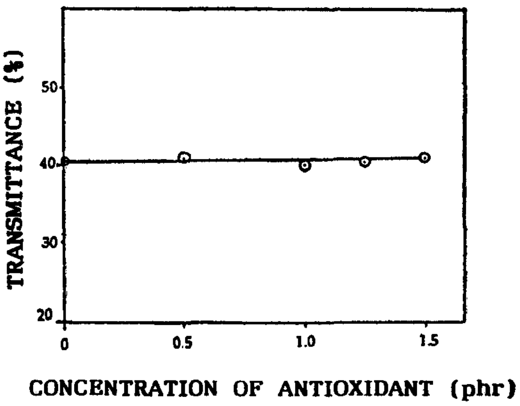

Fig. 7. Effect of concentration of antioxidant on transparency

For making dipped products from latex, methods like straight dipping, coagulant dipping and heat sensitized dipping are being practised. The thickness of the latex film obtained by the dipping process is affected by the viscosity of the compound especially in straight dipping. Viscosity modifiers are usually added to latex during compounding for increasing the viscosity of the compound. Effect of viscosity modifiers such as ammonium alginate, carboxymethyl cellulose, polyvinyl alcohol and casein at different concentrations, on transparency of latex films are depicted in Fig. 8. Polyvinyl

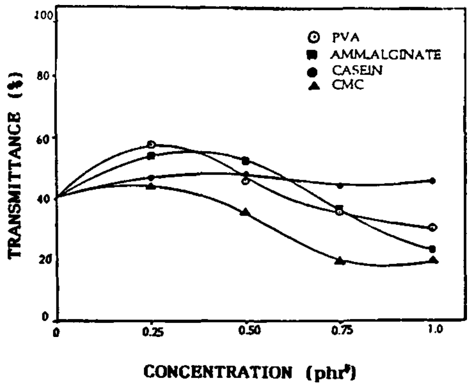

Fig. 8. Effect of concentration of viscosity modifiers on transparency

alcohol and ammonium alginate at 0.25 phr slightly improved transparency of the latex film and beyond this level transparency was found decreasing. But when casein was added, transparency of the film remained largely unaffected upto a concentration of 1 phr. However, in the case of carboxymethyl cellulose, transparency decreased beyond 0.25 phr. The decrease in transparency is believed to be due to the differences in refractive indices of the materials and that of rubber.

Fillers are added to natural rubber latex in order to modify its properties and to reduce cost. From Fig. 9, it is observed that all the fillers studied decreased transparency even at low concentrations, the maximum being in the case of titanium dioxide. The decrease was in the order titanium dioxide > whiting > china clay

> precipitated silica > magnesium carbonate. This decrease in transparency may be caused by the reflection and refraction of light by the filler particles. Transmission of light through a rubber compound will be decreased by fillers having a refractive index different from that of the rubber. If this difference is large, reflection and refraction will be larger and less light will be transmitted.

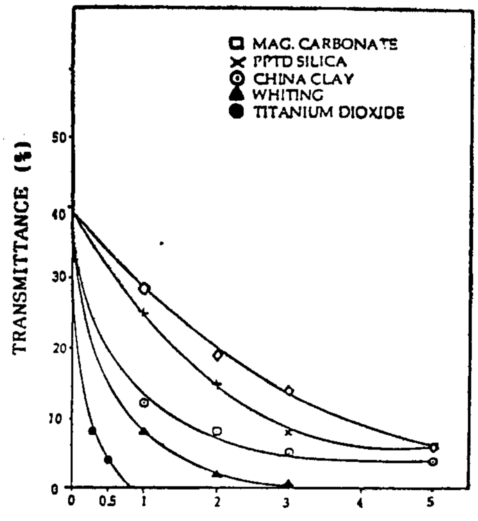

Fig. 9. Effect of concentration of fillers on transparency

Latex products are made either from centrifuged latex or from creamed latex. For preparing creamed latex, tamarind seed powder or ammonium alginate are usually used as creaming agents. It is seen that films made out of creamed latex prepared by using either tamarind seed powder or ammonium alginate and centrifuged latex had comparable transparency (Fig.10). Transparency was considerably reduced when field latex was used, indicating that the non-rubber constituents present in latex have a marked influence on the transparency of latex films.

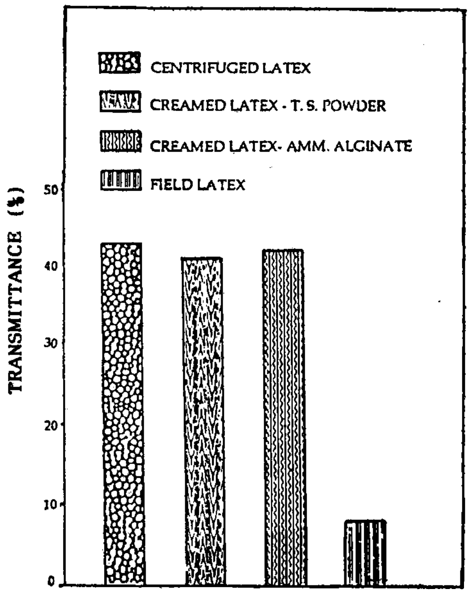

Fig. 10. Effect of type of latex on transparency

Prevulcanized latex is a very convenient material for the dipping industry. It can be used directly in the dipping operation, thus eliminating latex compounding and hence is especially attractive for the small scale latex goods manufacturers. The effect of prevulcanization and centrifugal clarification of the prevulcanized latex and heat treatment of the films made therefrom at 100°C for different periods is shown in Fig. 2. This shows that clarification of prevulcanized latex by centrifuging improves transparency of the films and a further enhancement in transparency is possible by heat treatment of the films. For obtaining better transparency heating of the films for a minimum period of 30 min at 100°C is required. Heating is reported to improve the technological properties of prevulcanized latex film (Gorton, 1979). Centrifuging of the prevulcanized latex effectively removes the unreacted ingredients and coagulum particles. Removal of these from the prevulcanized latex enables it to form a homogeneous film having good clarity.

During prevulcanization of latex, cross linking takes place mostly within individual rubber particles. Additional crosslinks are introduced in the prevulcanized latex film during heating, linking the coalesced rubber particles together covalently (Chapman and Porter, 1988). Instead of centrifuging the excess ingredients were allowed to settle down by keeping the prevulcanized latex undisturbed for different periods and then decanted out from which films were prepared and transparency measured after heating the films at 100°C for one hour. Results given in Fig. 11 show that removal of sedimentable impurities this way also improves transparency of the prevulcanized latex. In small scale manufacturing units where a centrifugal clarifier is not available it is possible to improve transparency by keeping the prevulcanized latex undisturbed for a sufficiently long period followed by decantation.

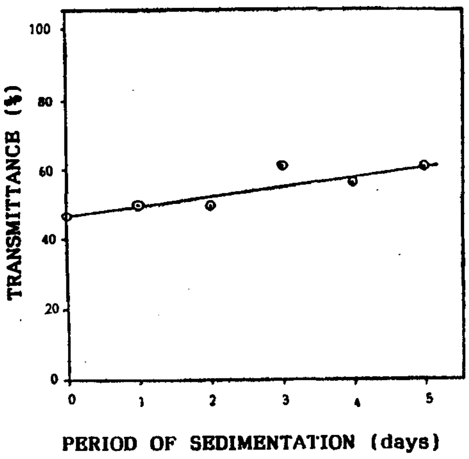

Fig. 11. Effect of clarification of prevulcanized latex on transparency

In the production of dipped rubber products coagulant dipping is usually practised. Coagulants significantly decreased transparency of latex vulcanizates. Among the coagulants studied, formic acid was found to have the minimum, and calcium nitrate the maximum, effect on transparency(Fig.12).

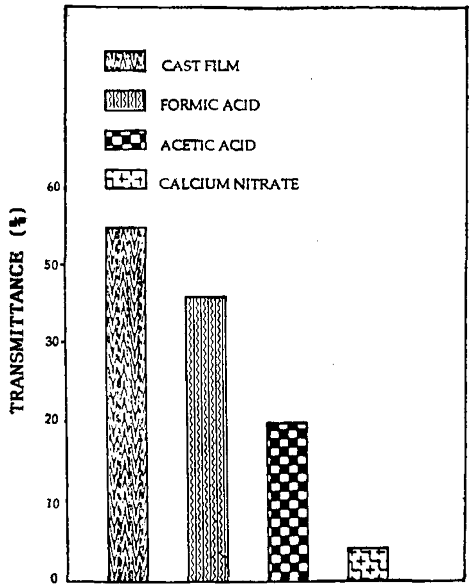

Fig. 12. Effect of coagulants on transparency

The effect of atmospheric humidity on transparency of latex vulcanizates (Fig. 13) shows that transparency is decreased by increase in humidity during storage. This is mainly due to the tendency of latex films to absorb moisture. The surface of natural rubber latex vulcanizates usually exhibits a degree of self tack. Tackiness is reduced by application of detackifiers. The effect of talc and dilute silicone emulsion as detackifiers, on transparency is shown in Table 2. It is observed that when talc is applied, the product is almost opaque. Better transparency and appearance is obtained with dilute silicone emulsion. It is reported that liquid detackifiers maintain or improve the shine on the surface of the latex articles (Gazeley *et al.*, 1988).

Table 2. **Effect of detackifier on film transparency**

Detackifier	Transmittance (%)
Without detackifier	40
Talc	0
Silicone emulsion	52

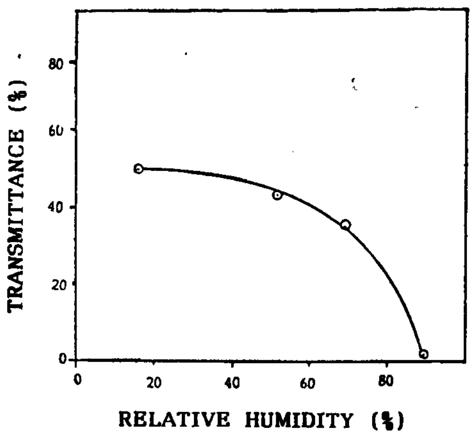

Fig. 13. Effect of relative humidity on transparency

Based on the results obtained, a formulation for preparing transparent rubber band was selected. The formulation is given in Table 3. As per the formulation, latex films (post vulcanized, prevulcanized and centrifugally clarified prevulcanized) were prepared. Films (post vulcanized) were also prepared using a conventional formulation (Table 4). All the films after drying at room temperature for 48 h were heated in an air oven for 1 h. The technological properties and retention of properties after ageing at 70°C for 96 h are shown in Tables 5 and 6, respectively. It was observed that all the films had comparable strength properties. The ageing properties were also comparable. Post vulcanized and prevulcanized films showed comparable transparency. Centrifugally clarified prevulcanized latex film exhibited the maximum transparency, while the film prepared from the conventional compound was opaque.

Table 3. **Formulation for transparent rubber band**

Ingredients	Parts by weight (wet)
60% Centrifuged latex (HA type)	167.0
10% Potassium hydroxide solution	2.5
50% Sulphur dispersion	2.0
50% Zinc diethyldithiocarbamate dispersion	2.0

Table 4. **A conventional rubber band formulation**

Ingredients	Parts by weight (wet)
60% Centrifuged latex (HA type)	167.0
50% Sulphur dispersion	2.4
50% Zinc diethyldithiocarbamate dispersion	2.0
50% Zinc oxide dispersion	0.4
33% Titanium dioxide dispersion	3.0

Table 5. **Technological properties**

Materials	Modulus, 100% (N/mm^2)	Modulus, 300% (N/mm^2)	Modulus, 600% (N/mm^2)	Tensile strength (N/mm^2)	Elongation at break (%)	Transmittance (%)
Post vulcanized film (Table 3)	0.77	1.21	2.40	22.2	1240	48
Prevulcanized film (Table 3)	0.74	1.20	2.37	20.9	1229	51
Centrifugally clarified prevulcanized film (Table 3)	0.71	1.05	2.29	20.1	1211	91
Post vulcanized film (Table 4)	0.79	1.32	2.58	21.6	1202	0

Table 6. **Retention (%) of properties after ageing at 70°C for 96 hours**

Materials	Modulus, 100%	Modulus, 300%	Modulus, 600%	Tensile strength	Elongation at break
Post vulcanized film (Table 3)	97.4	95.0	82.5	82.2	105.0
Prevulcanized film (Table 3)	97.2	93.3	80.5	95.6	110.0
Centrifugally clarified prevulcanized film (Table 3)	97.1	97.1	82.0	102.4	112.0
Post vulcanized film (Table 4)	93.6	94.6	89.5	82.0	97.15

SUMMARY AND CONCLUSIONS

For obtaining maximum transparency sulphur at the level of 1 phr shall be used and zinc oxide shall be omitted. Solid ingredients shall be added as fine dispersions. Paraffinic oil and antioxidant do not influence transparency of the vulcanizates significantly. Fillers shall be avoided. Centrifuged latex and creamed latex give comparable transparency to the films. A substantial increase in transparency is possible by clarification of prevulcanized latex preferably by centrifuging and by heat treatment of the films. Humidity decreases transparency. Products made by straight dipping method are more transparent than those made by coagulant dipping.

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