

A Study on the Use of Linseed Oil as Plasticiser in Natural Rubber Compounds

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Plasticisers such as minerals oils and synthetic oils were used in rubber compounds for improved processability, filler uptake and to reduce cost. Mechanical properties and thermal degradation of natural rubber compounds containing linseed oil had been studied to evaluate its suitability as a plasticiser. Naphthenic oil was used as a reference plasticiser. Tear strength, modulus, resilience and compression set of mixes containing linseed oil were improved compared with those containing naphthenic oil. Thermal studies showed an increase of 7°C in the temperature of initiation of degradation and an increase of 4°C in temperature at which peak rate of degradation occurred. The peak rate of degradation was comparable to that of the reference compound.

Key words: natural rubber; plasticiser; linseed oil; naphthenic oil; mechanical properties; thermal degradation

Plasticisers are low molecular weight non-volatile substances that are added to a polymer to improve its flexibility and processability. Even small quantities of plasticiser markedly reduces the glass transition temperature, T_g of the polymer. This effect is due to the reduction in cohesive forces between polymer chains. Plasticiser molecules penetrate into the polymer matrix and act as a lubricant between polymer chains, thereby reducing the T_g .

Plasticisers also improve filler dispersion and are useful in controlling the viscosity to desired levels. Generally used plasticisers include mineral oils, synthetic esters and some

of the natural products such as wood rosin and animal glue¹. Among these, the petroleum based oils are used extensively in rubber compounds. The fast depletion of petroleum resources calls for the exploration of alternatives as replacements. The vegetable oils are a potential alternative in this regard. The renewable nature of the source and the presence of other natural products such as tocopherol and free fatty acids can be advantageous in these applications.

Linseed oil is a widely used type amongst the drying oils, especially in the field of paints, varnishes and other coatings. A general

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modification that is usually carried out on unsaturated oils is epoxidation.

Thus epoxidised linseed oil (ELO) is generally accepted as a plasticiser for plastics and rubber. Aoki *et al.*² patented the use of ELO in SBR for heat stability. The reaction product of ELO with alpha and beta naphthylamine has been used in NR as a plasticiser and antioxidant. It decreases the viscosity, does not bloom and disperses well in NR³. Dynamically crosslinked thermoplastic nitrile rubber blends with good processability and physical properties have been prepared by the addition of about 2 p.h.r. ELO⁴. Aniline and phenyl hydrazine modified ELO are used as multipurpose ingredients in NR and NBR. They act as plasticiser, accelerator and antioxidant. There are a few examples, where derivatives other than epoxide have also been used as plasticiser, *eg.* linseed oil methyl ester diacetal⁵. Acetoxy methyl, derivative of linseed oil as a plasticiser in PVC can give equal or superior properties compared to conventional diester plasticisers⁶.

Linseed oil as such is used as a plasticiser in a few elastomers. A 10-15 p.h.r. loading of linseed oil in vulcanisates of Neoprene rubbers, showed a heat resistance of > 500 hr at 120°C and > 50 hr at 150°C⁷. Soya bean oil and rape oil also showed this property. Heat and ozone resistance of chloroprene rubber compounds with modified linseed oil (3-3.5 p.h.r.) was also reported⁸. Vulcanisate properties of Neoprene and 1:1 blend of *cis* 1,4 butadiene with linseed and other oils were evaluated by Velchewa *et al.*⁹ Plant oils were found to have a better plasticising effect than mineral oils or DOS and also imparted better low temperature flexibility.

Epoxidised linseed oil has been used as a vulcanising agent in carboxylated nitrile rubber (XNBR)-ionomer blends¹⁰. Linseed oil as such

was used as a multipurpose additive in NBR to improve its mechanical properties and processability and to reduce cure time¹¹. Soybean oil was used as a plasticiser in natural rubber(NR)¹² and as a plasticising agent in cold vulcanised rubber¹³. Blown soya bean oil was used as a plasticiser in ester gums¹⁴. Castor oil has been used as a plasticiser in nitrocellulose¹⁵ in polystyrene films¹⁶, in rubbers containing acrylonitrile and styrene¹⁷, and in NR to enhance certain mechanical properties.

In the present study, we have used linseed oil as a plasticiser in a typical natural rubber compound containing 45 p.h.r. of carbon black. Mechanical properties and thermal characteristics of these compounds were compared with that of the control compound containing naphthenic oil.

EXPERIMENTAL

Materials

Natural rubber (ISNR 5) was obtained from the Rubber Research Institute of India, Kottayam. Zinc oxide and stearic acid were supplied by M/s. Meta Zinc Ltd., Mumbai and Godrej Soaps (Pvt) Ltd., Mumbai, respectively.

Mercaptobenzthiazyl disulphide (MBTS) and tetramethylthiuramdisulphide (TMTD) were supplied by Bayer Chemicals, Mumbai and Polylefins Industries Ltd., Mumbai, respectively. Sulphur was supplied by Standard Chemical Company, Pvt. Ltd., Chennai. Carbon black (HAF N-330) used in the study was supplied by M/s Philips Carbon, Kolkata.

Naphthenic oil obtained from Hindustan Petroleum Ltd., Mumbai, having the following specification: specific gravity – 0.98; aniline

point – 78°C and Viscosity Gravity Constant – 0.87.

Linseed oil was of commercial grade and obtained from the local market. Linseed oil is a typical drying oil widely used in paints and varnishes. The major fatty acids present in the oil are oleic acid – 16%, linoleic acid – 14.2% and linolenic acid – 60%, palmitic acid – 5% and stearic acid – 3%. The oil also contains small amounts of tocopherols and phosphatides; these materials are said to have antioxidant properties.

The following are the characteristics of linseed oil:

- Viscosity gravity constant: 0.8756
- Specific gravity : 0.935
- Iodine value : 170-185
- Saponification value : 188-196
- Refractive index at 25°C : 1.4805-1.4825

Processing

The formulation of the mixes is given in Table 1.

The mixes were prepared on a laboratory sized two-roll mill (16 cm × 33 cm) using a friction ratio of 1:1.25 as per procedure given in *ASTM D 3184-89 (2001)* over a time period of 18 min. Cure characteristics at 150°C were determined using Goettfert Elastograph Model (67.85). Tensile properties such as tensile strength and tear strength were measured according to *ASTM D 412* and *ASTM D 624*, respectively using the Shimadzu Universal Testing Machine model AG 50 kN.

The hardness (Shore A) of the samples was determined using Zwick 3114 hardness tester according to *ASTM D 2240-86*. Samples with dimensions of 12 mm diameter and minimum 6 mm thickness were used. A load of 12.5 N was applied and the readings taken 10 seconds after the indenter had made a firm contact with the specimen.

The flex resistance of the vulcanisates was determined using a Wallace De Mattia flexing machine as per *ASTM D 430-57 T*.

Abrasion resistance of the samples was measured using a DIN abrader based on *DIN*

TABLE 1. COMPOUND FORMULATION (p.h.r.)

Ingredients	Mix number										
	L ₀	L ₂	L ₄	L ₆	L ₈	L ₁₀	N ₂	N ₄	N ₆	N ₈	N ₁₀
Natural Rubber	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
Vulcanox HS®	1	1	1	1	1	1	1	1	1	1	1
Vulcanox 4020®	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MBTS	1	1	1	1	1	1	1	1	1	1	1
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
HAF	45	45	45	45	45	45	45	45	45	45	45
Linseed oil (L)	0	2	4	6	8	10	–	–	–	–	–
Naphthenic oil (N)	–	–	–	–	–	–	2	4	6	8	10
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

53516. The results were expressed as volume loss per hour.

$$V = \frac{\Delta M \times 27.27}{\rho} \quad \dots 1$$

where,

V = Abrasion loss in cc/hr,

ΔM = Mass loss and

ρ = Density of the sample.

Rebound resilience was determined using a vertical rebound method according to *ASTM D 2832-88*.

Heat build-up was tested on a Goodrich Flexometer as per *ASTM D 623-78* (Method A). The samples were 25 mm in height and 19 mm in diameter. The oven temperature was kept constant at 50°C. The stroke was adjusted to 4.45 mm and the load to 10.05 kN.

Compression set at constant strain was measured according to *ASTM D 395-86* (Method B). Essentially samples of 6.25 mm thickness and 18 mm diameter were compressed to constant strain (25%) for 22h in an air oven at 70°C. At the end of the test period the test specimens were removed from the compression ring and allowed to recover freely at room temperature for 30 minutes and the final thickness measured. The compression set, expressed as a percentage, was calculated using the following expression.

$$\text{Compression set (\%)} = \frac{T_i - T_f}{T_i - T_s} \times 100 \quad \dots 2$$

Where T_i and T_f are the initial and the final thickness of the specimen, respectively and T_s is the thickness of the space bar used.

Thermal Analysis

Thermogravimetric analysis of the specimens was carried out on the Universal V4 2E, TA Instrument, using a heating rate of 10°C/min under nitrogen. The following characteristics were determined from the thermogravimetric curves: the temperature of onset of degradation; the temperature at peak rate of decomposition; the peak rate of degradation and the weight of residue remaining at 600°C.

RESULTS AND DISCUSSION

Figure 1 shows the variation of cure time with oil loading. While the cure time decreases with the concentration of linseed oil the cure rate (*Figure 2*) shows a corresponding increase. The cure time was reduced by 0.4 min and the cure rate was increased by 0.02 Nm/min at a 6 p.h.r. level. There was a slight increase in the scorch time (*Figure 3*) at all oil loadings. Even with a delayed start of the cure reaction, the cure time was not affected apparently due to the higher rate of cure reaction.

The $T_{(\text{max-min})}$ an indication of the stiffness of the compound after curing (*Figure 4*), shows that all the mixes had higher stiffness at high oil loading, as expected. *Figure 5* shows that the crosslink density of linseed oil mixes was higher compared to naphthenic oil mixes. The higher torque may also be due to better filler-matrix interaction resulting from better dispersion.

Figure 6 gives the variation of the tensile strength of the vulcanisates with different oil loadings. Linseed oil showed better tensile strength values when compared with the control mix. The maximum tensile strength

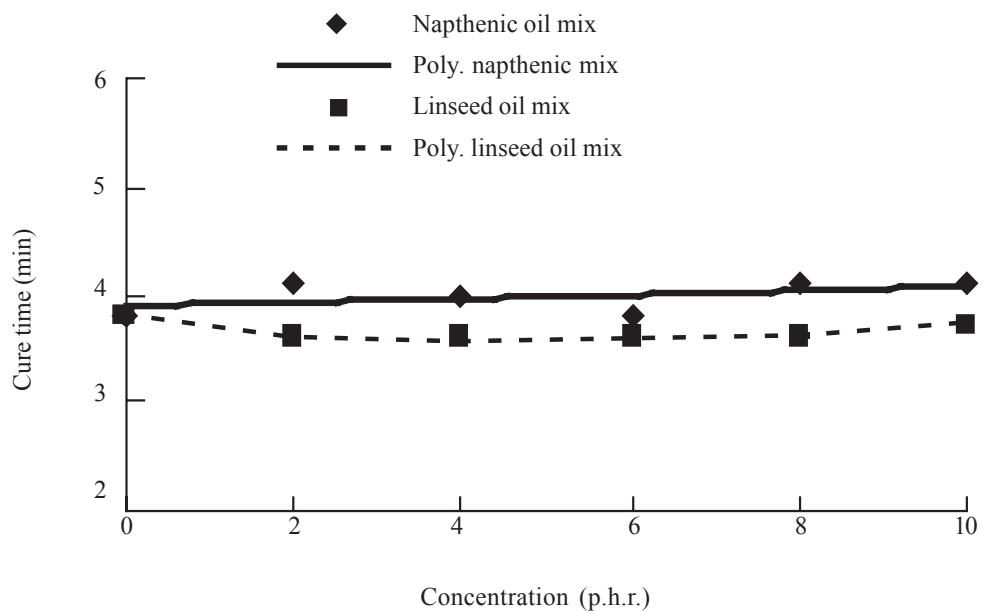


Figure 1. Variation of cure time with oil content.

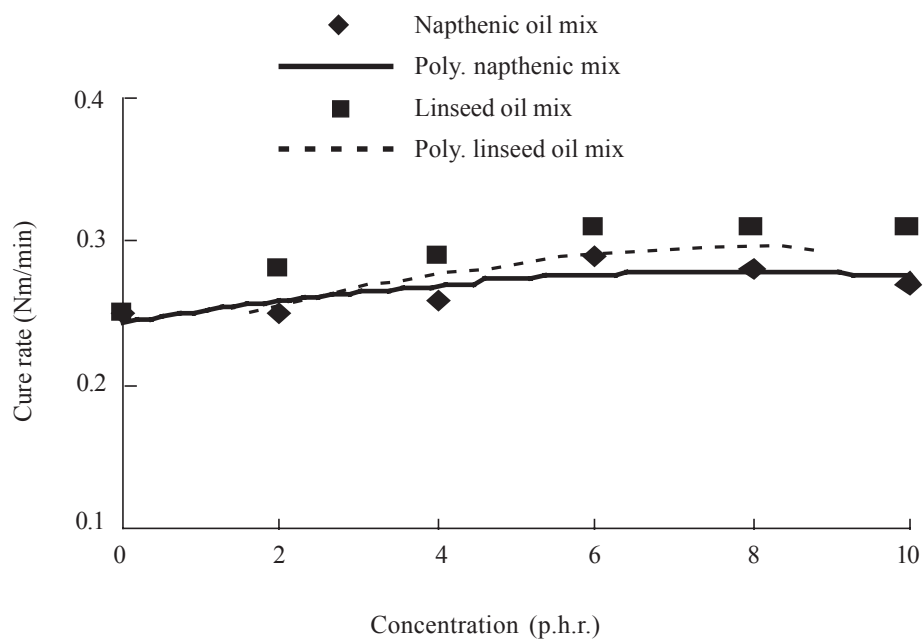


Figure 2. Variation of cure rate with oil content.

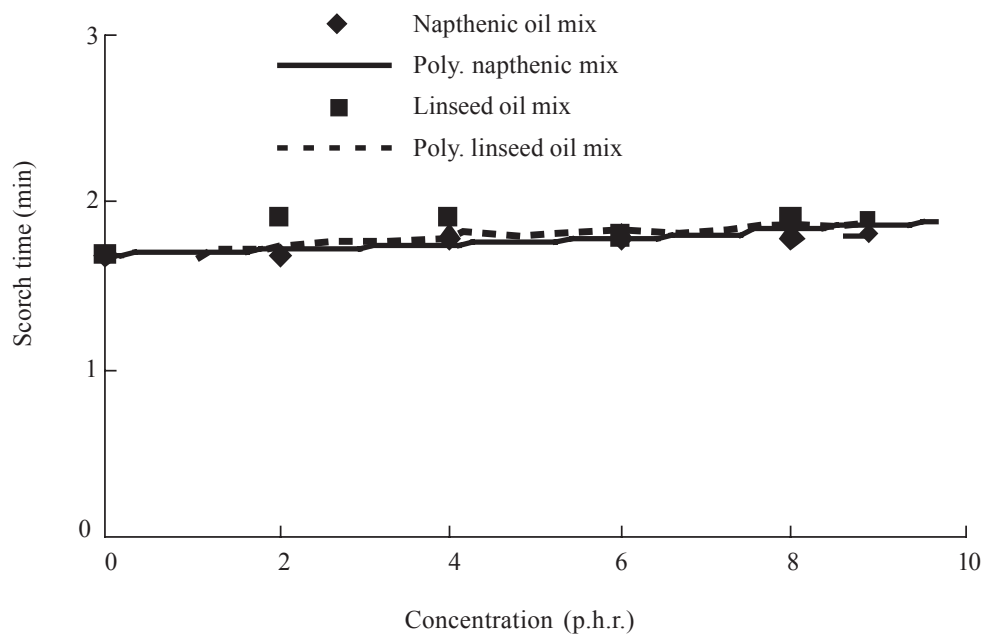


Figure 3. Variation of scorch time with oil content.

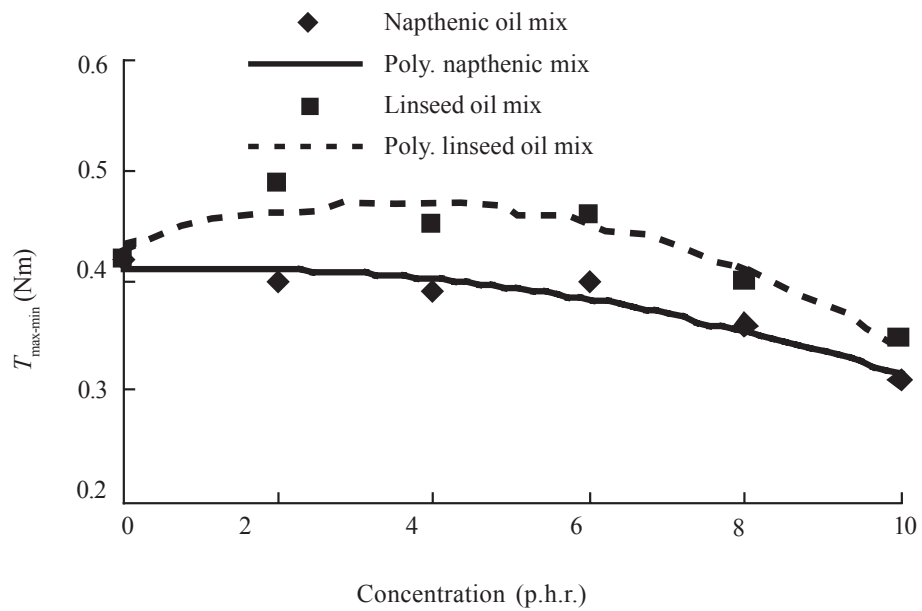


Figure 4. Variation of $T_{max-min}$ with oil content.

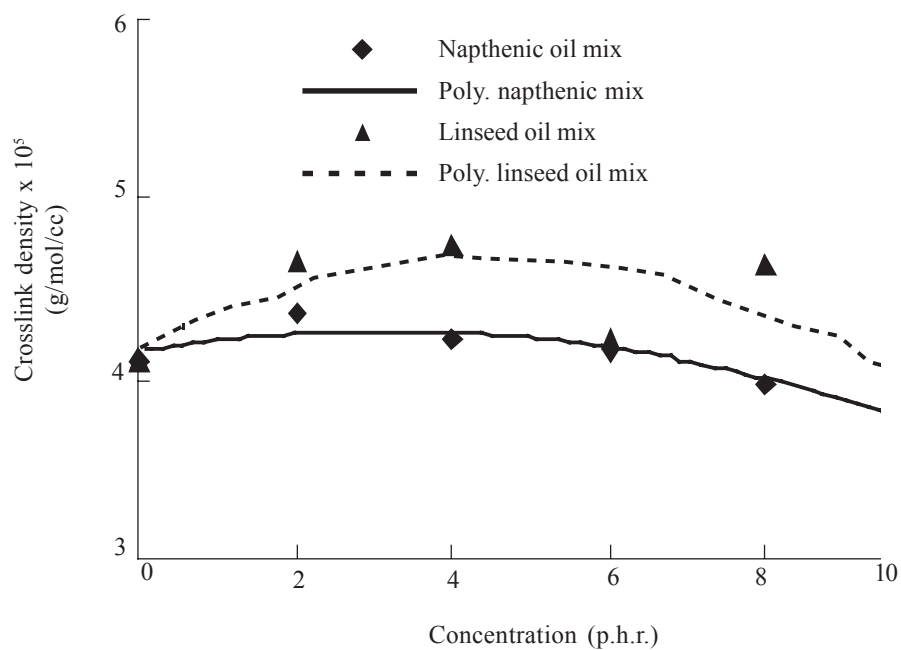


Figure 5. Variation of crosslink density with oil content.

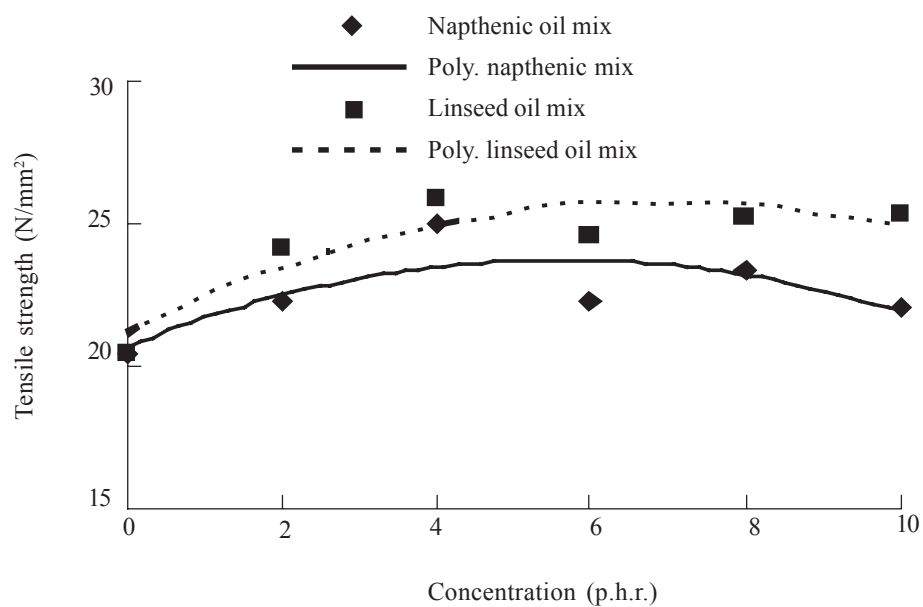


Figure 6. Variation of tensile strength with oil content.

was obtained at 6 p.h.r. oil loading. The tensile strength was improved by 7% at 6 p.h.r. loading of linseed oil. Better strength was obtained when the filler was dispersed homogeneously in the matrix. At lower oil loading, the filler dispersion was non-uniform and hence the strength was not fully developed.

Figures 7 and 8 compare the modulus and elongation at break of the vulcanisates. The modulus of the linseed oil mixes was found to be better than the control compound which was in agreement with crosslink density values. The ultimate elongation was lower for linseed oil mixes.

The ageing resistance of vulcanisates with linseed oil was better than the control mix with naphthenic oil (*Table 2*). The higher ageing resistance of vulcanisates with linseed oil may be due to the presence of natural antioxidants in it. The vulcanisate without plasticiser showed poor ageing resistance.

The tear strength values show a significant increase in the case of linseed oil (*Figure 9*) at all oil loadings. In the case of naphthenic oil the tear strength remained constant.

Hardness, a measure of low strain elastic modulus was higher (*Figure 10*) for linseed oil mixes, compared to the control mix containing naphthenic oil. As the hardness increased, abrasion loss, which was a measure of reinforcement, decreased (*Figure 11*). Both the values were in agreement with higher crosslink density of linseed oil mixes.

The rebound resilience (*Figure 12*) of the vulcanisates was found to be improved when linseed oil substitutes naphthenic oil. Linseed oil showed higher flex crack resistance (*Table 2*) compared to the control mix containing naphthenic oil. Compression set values (*Figure 13*) was lower than the control mix. This can be attributed to higher crosslink density. Heat build up (*Figure 14*) was comparable with the naphthenic oil mixes.

TABLE 2. FLEX CRACKING AND AGEING RESISTANCE OF THE VULCANISATES

Mix No	Flex cracking resistance (lakhs of cycles)	Retention in tensile strength (%)
L ₀	1.1	41
L ₂	1.2	58
L ₄	3.5	67
L ₆	5.1	60
L ₈	6.2	74
L ₁₀	6.5	76
N ₂	1.6	51
N ₄	2.4	57
N ₆	2.8	66
N ₈	3.9	69
N ₁₀	5.8	52

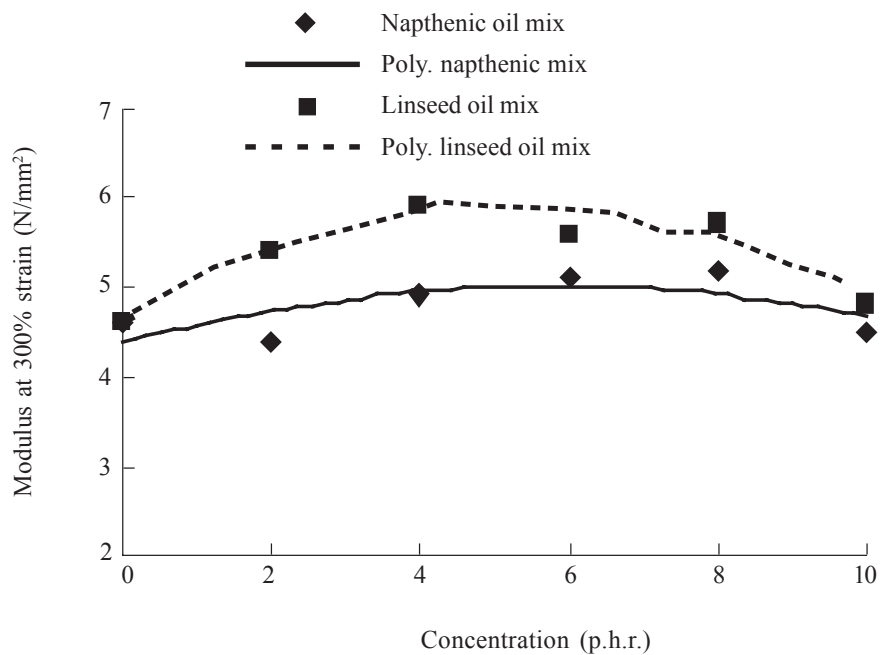


Figure 7. Variation of modulus with oil content.

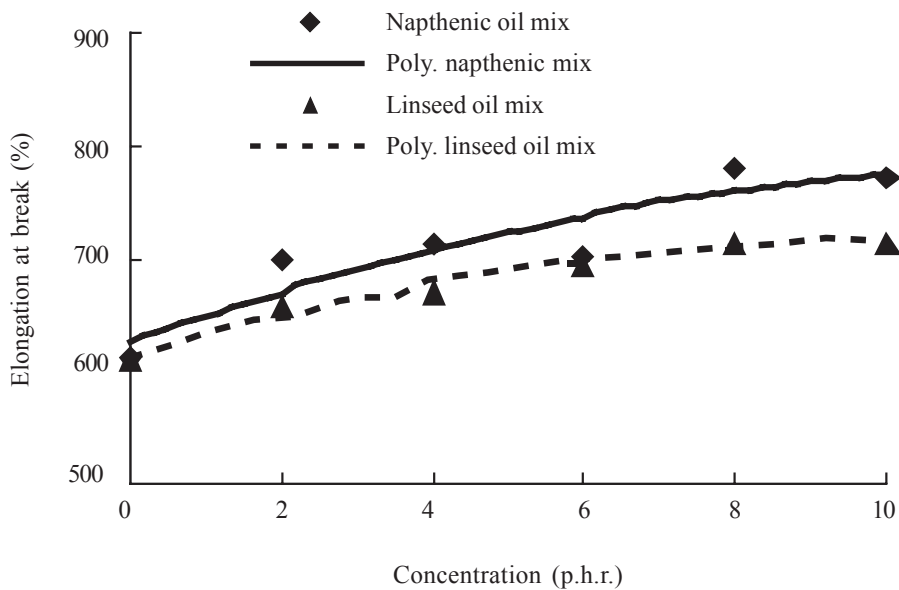


Figure 8. Variation of elongation at break with oil content.

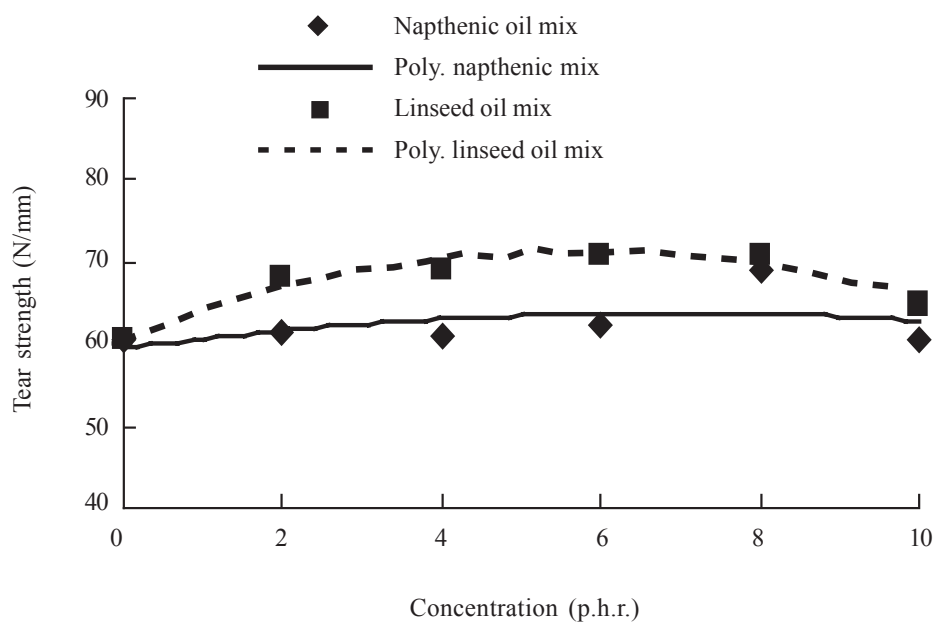


Figure 9. Variation of tear strength with oil content.

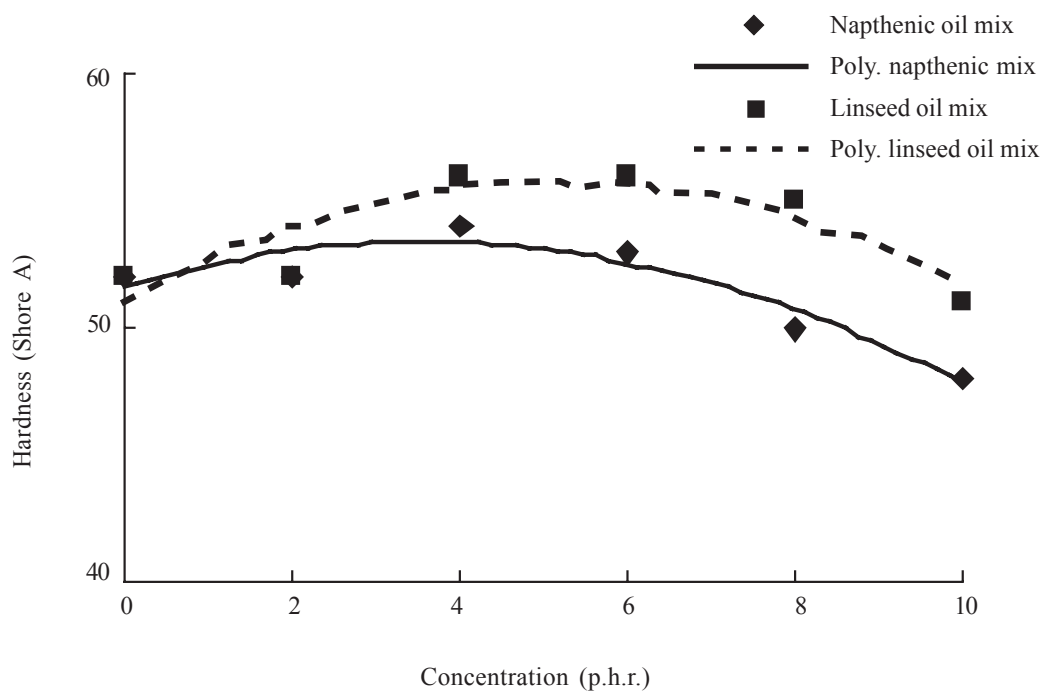


Figure 10. Variation of hardness with oil content.

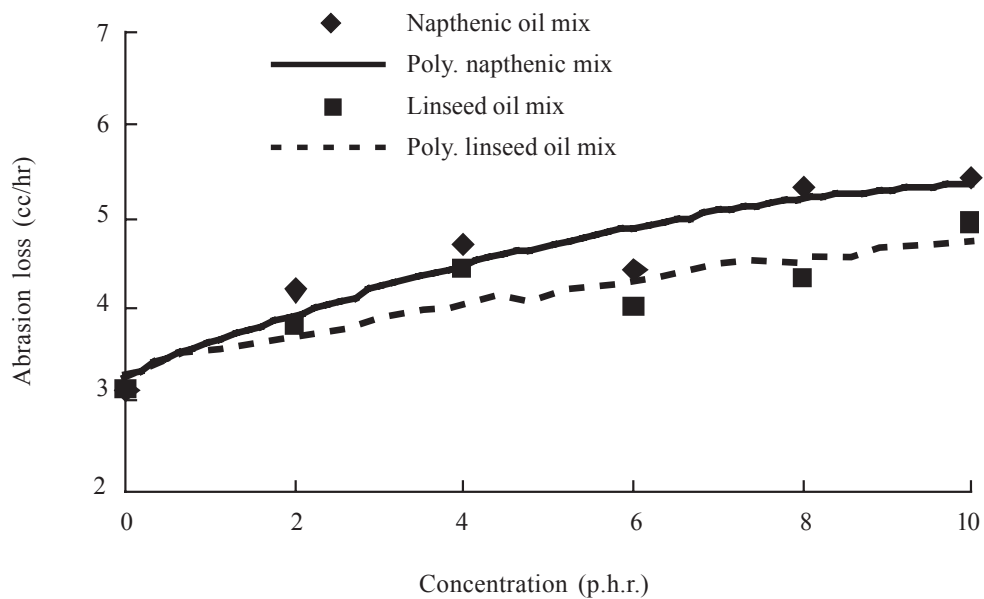


Figure 11. Variation of abrasion loss with oil content.

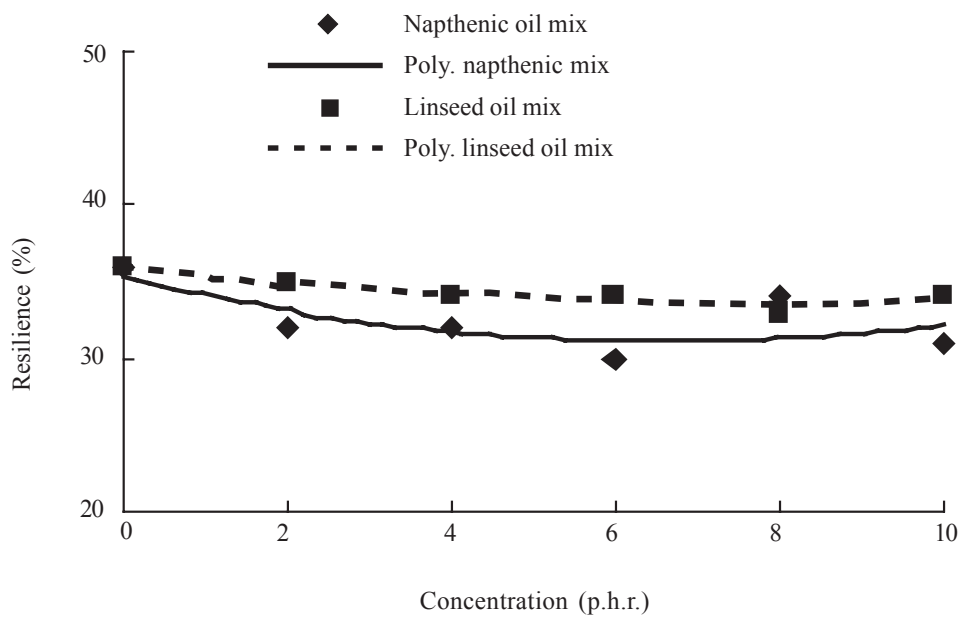


Figure 12. Variation of resilience with oil content.

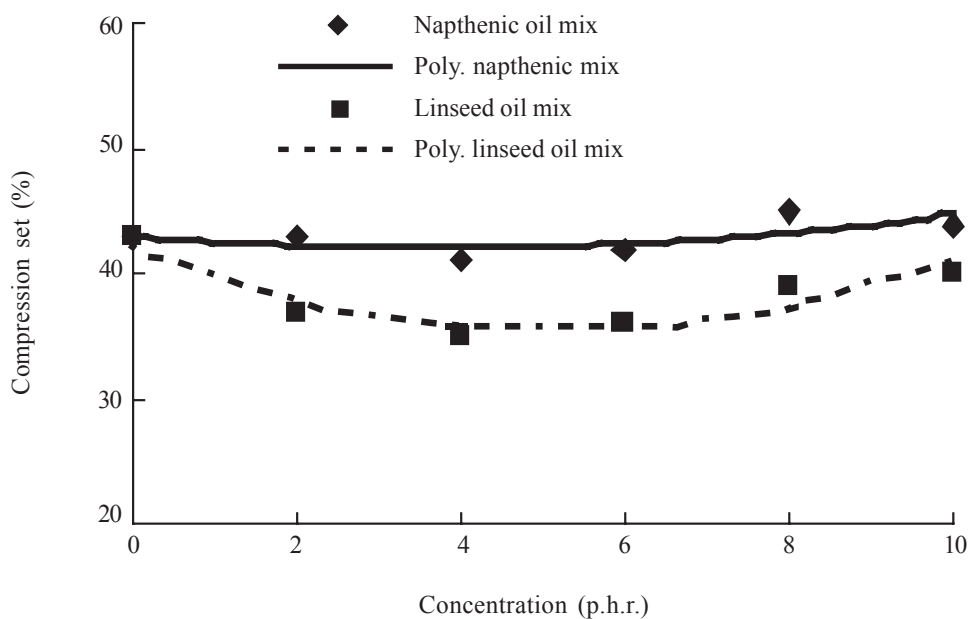


Figure 13. Variation of compression set with oil content.

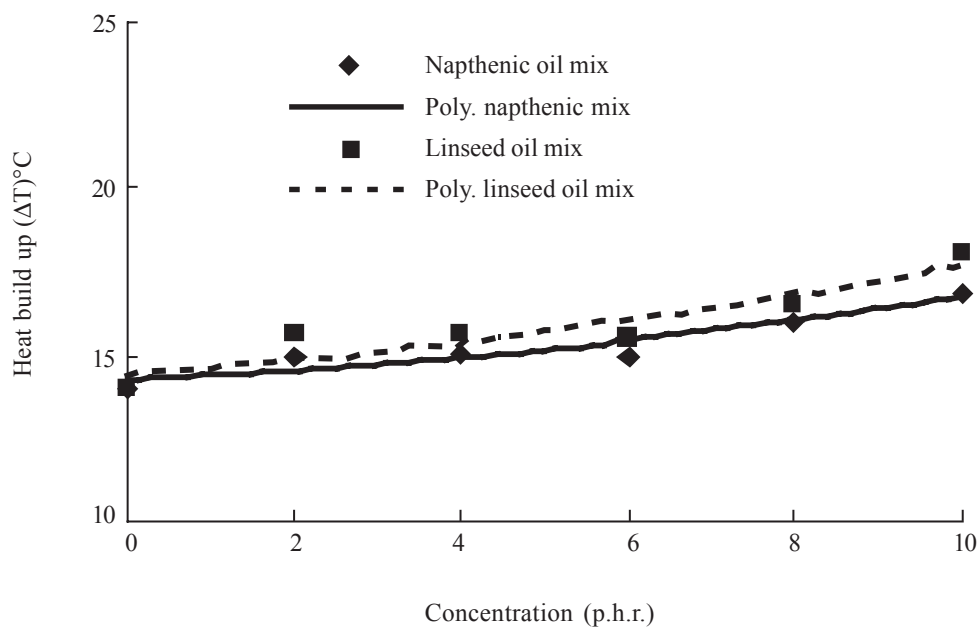


Figure 14. Variation of heat build up with oil content.

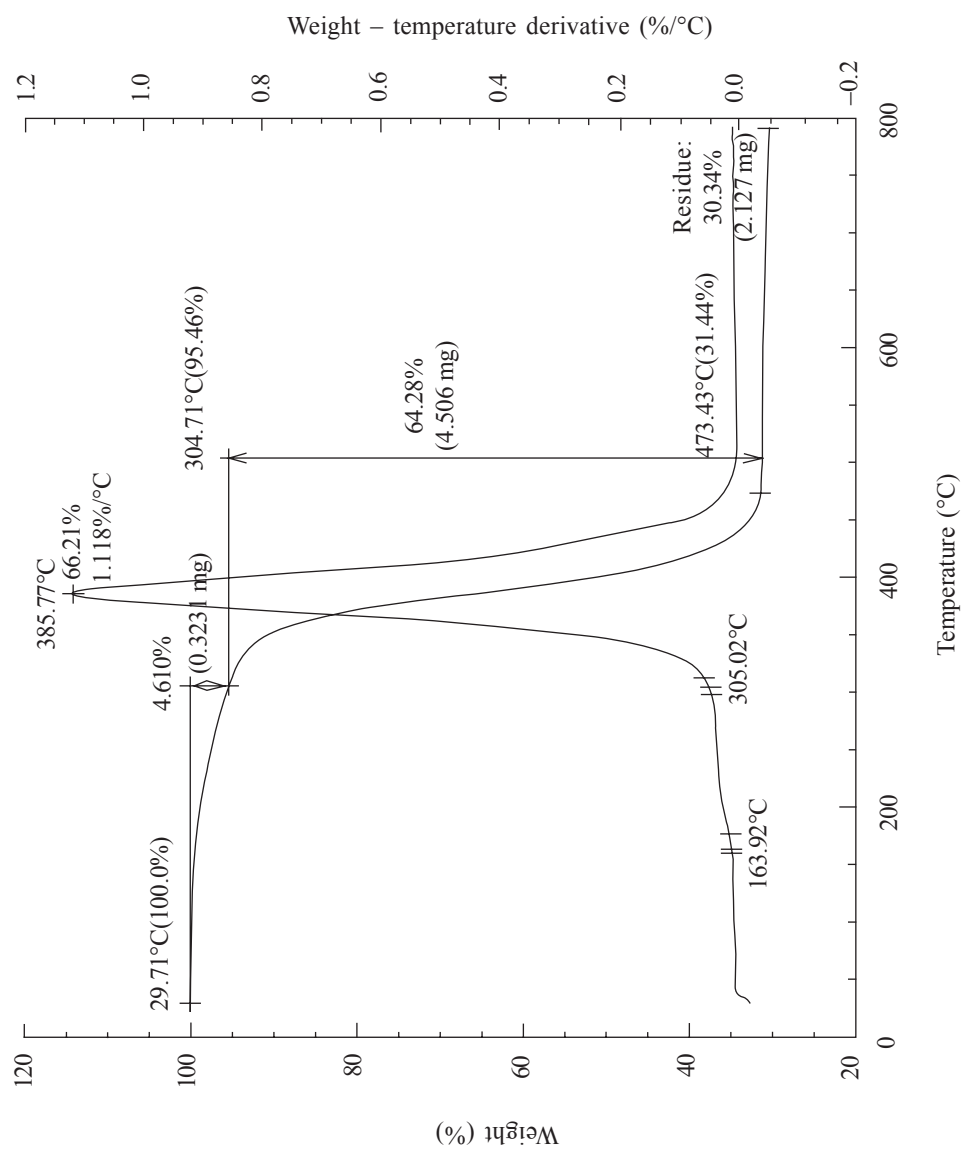


Figure 15a. Thermogravimetric curve of mix with (4 p.h.r.) linseed oil.

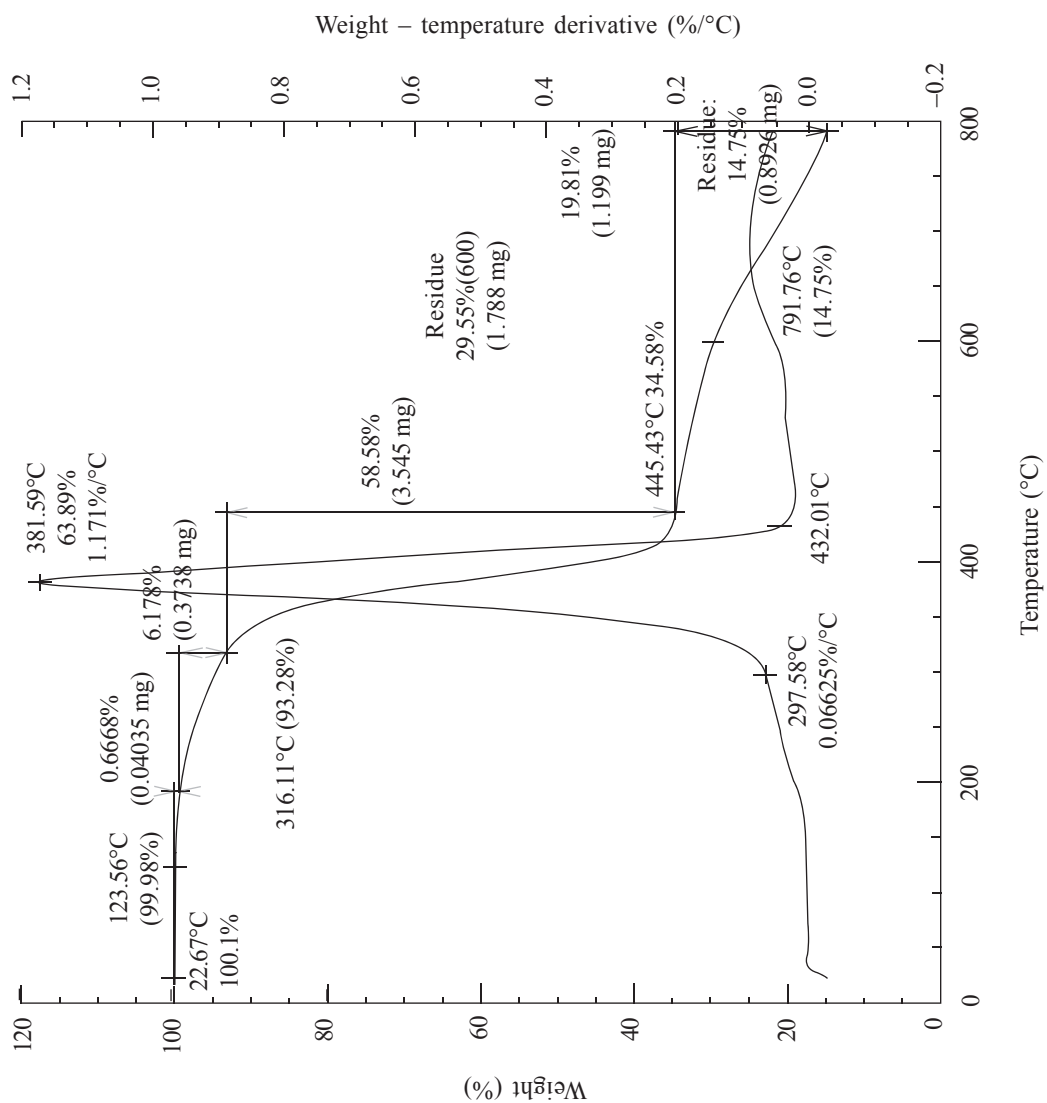


Figure 15b. Thermogravimetric curve of mix with (4 p.h.r.) naphthenic oil.

TABLE 3. THERMAL DEGRADATION CHARACTERISTICS OF MIXES L₄ AND N₄

Mix	Temperature of initiation (T _i), °C	Peak degradation temperature (T _{PD}), (°C)	Peak rate of decomposition (R _{PD}), (% / min)	Residue at 600°C, (%)
L ₄	305	386	1.12	31.4
N ₄	298	382	1.17	29.6

Figures 15a and 15b show the thermogram of mixes with linseed oil and naphthenic oil, respectively at 4 p.h.r. concentration. Improvement in thermal stability was evident from the higher temperature of initiation (by 7°C) and higher peak degradation temperature (by 4°C) given in (Table 3). It also shows a relatively lower rate of degradation and higher residual weight. The improved thermal stability of the linseed oil mixes may be due to better crosslink density and natural antioxidants.

CONCLUSIONS

From the study, the following conclusions may be drawn. Linseed oil can be used as an alternative plasticiser in natural rubber compounds. Tensile strength, tear strength, modulus, resilience and compression set were better compared to naphthenic oil mixes. Hysteresis properties were comparable. The linseed oil mix also showed higher thermal stability when compared with the control mix. Based on these results it was reasonable to conclude that linseed oil can be used in place of other conventional process aid in NR vulcanisation systems with not much adverse effects on processing parameters, cure characteristics and vulcanisate physical properties.

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