

1. Report No. <b>298</b>	2. Government Accession No.	3. Recipients Catalog No.	
4. Title and Subtitle <b>Enhancing and Standardizing Interaction of Rubber Particles with Asphalt</b>		5. Report Date	
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9. Performing Organization Name and Address <b>Department of Chemistry Louisiana State University Baton Rouge, LA 70803-1804</b>		8. Performing Organization Report No.	
12. Sponsoring Agency Name and Address <b>Louisiana Department of Transportation and Development PO Box 94245 Baton Rouge, LA 70804-9245</b>		10. Work Unit No. <b>95-1B</b>	
15. Supplemental Notes <b>Conducted in Cooperation with the U. S. Department of Transportation, Federal Highway Administration</b>		11. Contract or Grant No.	
16. Abstract <b>Addition of ground rubber particles to asphalt can enhance several fold the stiffness of the blend as reflected by <math>G^*/\sin \delta</math> of the rubber-asphalt cements (RAC). Pretreatment of rubber particles with as little as 5% aromatic oil (AO) enhances the apparent compatibility of rubber with asphalt at moderate temperatures; the enhanced stiffness of the blend is retained. The most successful protocol for adding aromatic oil involves preblending of the oil with rubber before mixing with asphalt. Oil addition facilitated preparation of RAC's with 15% rubber that exhibit <math>\eta @ 135^\circ\text{C}</math> less than 3.0 Pa.s. AC-10 and AC-30 asphalt binders were blended with crumb rubber (CR) presoaked in AO and acceptable SHRP spec requirements were observed for each blends. Blends of AC-10 with 15% CR and 5% AO met the SHRP specs @ 64C while blends of AC-30 with 15% CR and 15% AO met the specs @ 70C. Measurement of mix stiffness using <math>G^*/\sin\delta</math> at high temperatures was not possible due to inverse behavior of <math>\sin\delta</math> with temperature. The low temperature stiffness of these blends met the specifications @ -12C (bending beam test). TFOT and PAV aging studies reveal that aromatic oil addition does not completely alleviate phase separation, but the aged blends retain satisfactory viscoelastic properties.</b>		13. Type of Report and Period Covered <b>Final Report 10/01/94-6/30/95</b>	
17. Key Words <b>Asphalt/rubber blends, asphalt/rubber/aromatic oils blends, SHRP specs, dynamic mechanical analysis, TFOT aging, PAV aging, phase separation of aged blends</b>		18. Distribution Statement	
19. Security Classification (of this report) <b>None</b>	20. Security Classification (of this page) <b>None</b>	21. No. of Pages <b>54</b>	22. Price <b>N/A</b>

ENHANCING AND STANDARDIZING INTERACTION OF  
RUBBER PARTICLES WITH ASPHALT

FINAL REPORT

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CONDUCTED FOR

LOUISIANA DEPARTMENT OF TRANSPORTATION AND DEVELOPMENT  
LOUISIANA TRANSPORTATION RESEARCH CENTER  
in Cooperation with  
U. S. DEPARTMENT OF TRANSPORTATION  
FEDERAL HIGHWAY ADMINISTRATION

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NOVEMBER, 1995

## ABSTRACT

Addition of ground rubber particles to asphalt can enhance several fold the stiffness of the blend as reflected by  $G^*/\sin \delta$  of the rubber-asphalt cements (RAC). Pretreatment of rubber particles with as little as 5% aromatic oil (AO) enhances the apparent compatibility of rubber with asphalt at moderate temperatures; the enhanced stiffness of the blend is retained. The most successful protocol for adding aromatic oil involves preblending of the oil with rubber before mixing with asphalt. Oil addition facilitated preparation of RAC's with 15% rubber that exhibit  $\eta @ 135^\circ\text{C}$  less than 3.0 Pa•s. AC-10 and AC-30 asphalt binders were blended with crumb rubber (CR) presoaked in AO and acceptable SHRP spec requirements were observed for each blends. Blends of AC-10 with 15% CR and 5% AO met the SHRP specs @  $64^\circ\text{C}$  while blends of AC-30 with 15% CR and 15% AO met the specs @  $70^\circ\text{C}$ . Measurement of mix stiffness using  $G^*/\sin \delta$  at high temperatures was not possible due to inverse behavior of  $\sin \delta$  with temperature. The low temperature stiffness of these blends met the specifications @  $-12^\circ\text{C}$  (bending beam test). TFOT and PAV aging studies reveal that aromatic oil addition does not completely alleviate phase separation, but the aged blends retain satisfactory viscoelastic properties.

## IMPLEMENTATION STATEMENT

This study encompassed exploratory work to examine the procedures for producing stable rubber particles/asphalt blends by pre-wetting the rubber with aromatic oils to enhance the compatibility between rubber and asphalt. As such, there are no directly implementable results. However there are some major findings which should be considered in preparing and storing asphalt/rubber blends, i.e. blends containing greater than 10% crumb rubber are not stable and tend to separate rapidly when held at high temperatures, unless the rubber particles are pre-soaked in thermally stable aromatic oils. Further exploration could lead to less expensive, easier to handle rubberized asphalt cements which would be more stable.

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## LIST OF ACRONYMS

AC	Asphalt Cement
RAC	Rubber Asphalt Cements
G	Shear Modulus
sin	Sine
$\delta$	Loss Angle
Pa	Pascal
$\eta$	Viscosity
TFOT	Thin Film Oven Test
CR	Crumb Rubber
AO	Aromatic Oil
SHRP	Strategic Highway Research Program
DMA	Dynamic Mechanical Analysis
Sec or s	Second
PAV	Pressure Aging Vessel
°C	Celsius Degree
i.e.	That Is ( <i>Id est, Latin</i> )
G*	Complex Shear Modulus
G'	Shear Storage Modulus
G''	Shear Loss Modulus
PR	Powder Rubber
Gal	Gallon
TG	Thermo-Gravimetry
DTA	Differential Thermal Analysis
mg	Milligram
cP	Centi Poise
Hz	Herz
DSR	Dynamic Shear Rheometer
rad	Radian
RTFO	Rolling Thin Film Oven
mm	Millimeter
min	Minute
mL	Milliliter
kPa	Kilo Pascal
BBR	Bending Beam Rheometer
S(t)	Creep Stiffness @ Time <i>t</i>
<i>m</i>	Creep Rate
rpm	Rotations per Minute

## INTRODUCTION

### BACKGROUND

Asphalt, or the asphalt cement (AC), the residues left after distillation of the more volatile fractions of crude oil, is the most versatile material available for applications in road constructions. From the chemical point of view, asphalts are considered to be composed of polar asphaltenes and neutral maltenes. The resins from maltenes disperse the asphaltenes in the oils to provide a microscopically homogeneous liquid and thus the asphalt may be considered a colloidal systems in which micelles are dispersed in a continuous phase of oil. The most important parameter governing the success of a polymer modifier in asphalt is its compatibility. The introduction of any incompatible polymer under agitation into such a colloidal system at high temperature generally results in asphaltene flocculation and oil bleeding, leading to a binder having no cohesion [1].

Compatibilized rubber modifies the asphalt to improve especially the low temperature ductility, elasticity and cyclic loading properties of the mixture. Additional property improvements include adhesion and tack, durability, softening point and cold flow, impact resistance, resilience and toughness. These properties have been achieved using styrene-butadiene block copolymers, but comparable property improvements have not been observed with crumb rubber asphalt blends (RAC's).

The usual procedure for preparing RAC's involves adding rubber particles to molten asphalt. In a previous investigation [2], blends with up to 20% ground vulcanized rubber (both crumb and 200 mesh powder particles) from recycled tires were prepared with asphalt cements of various grades (AC5 - AC30) and evaluated using dynamic mechanical analysis, DMA. Blends produced from powdered rubber particles exhibited Newtonian behavior at high temperatures, similar behavior was not observed with crumb rubber blends. The mechanical properties of asphalt-rubber blends depended upon the concentration of rubber additives, the particle dimensions, and the chemical composition of the asphalt.



Some asphalts induced excessive swelling of the rubber particles; resulting in 135°C viscosities greater than SHRP recommended 3 Pa•Sec. Aging of the asphalt rubber blends revealed a significant difference between crumb rubber and powdered rubber additives. Blends with powdered rubber appeared to remain compatible or at least partially compatible through the aging process in the pressure aging vessel, PAV, and the blends retained the physical properties associated with the additive. The DMA data suggested that the low temperature cracking resistance of these blends was enhanced. In contrast, simple blends of crumb rubber with asphalts ranging in grade from AC5 to AC30 exhibited phase separation during the thin film oven aging test (TFOT). These blends lost all the physical property enhancement contributed by the rubber additive. The main reason for this gross incompatibility seemed to be the absorption of light fractions and the subsequent breaking of the colloidal equilibrium. The result, as mentioned before, was the asphaltene flocculation and oil bleeding, leading to a binder having little or no cohesion. It is therefore the aim of the present study to address this shortcoming by using specific additives, such as presoaking aromatic oils, to prevent the excessive absorption of lights by rubber and the consequent breaking of colloidal equilibrium.

A further area impacted by incorporating crumb rubber into asphalt cements is the recyclability of these mixes [3]. If a ton of asphalt containing 20 lb. (one tire) of crumb rubber cannot be recycled, a twenty pound problem has been multiplied 100 fold. It is foreseen that the aromatic oils will not affect negatively the recycling of RAC's since they will be assimilated by AC as a maltene component. More research is required however before the legislated minimum utilization standards [4] are implemented.

Extensive research has been done over the last decade in studying the rheology of asphalt and asphalt concrete [5]. The implementation of the performance-related specifications for asphalt cements [6] developed by the Strategic Highway Research Program (SHRP) gave a strong impetus for a thorough investigation of rheological behavior of asphalt binders [7-9]. Dynamic

shear tests are advantageous because the data can be acquired within the linear range of the asphalt in a loading mode that is similar to that of traffic loading. These measurements are particularly useful in the transition region where delayed elasticity is a major portion of the material response [7].

## **GENERAL DATA ON MIXING RUBBER IN ASPHALT.**

The full potential of rubber in asphalt cannot be realized unless adequate mixing under good quality control is performed [10]. Both viscosity (60°C) and ductility at low temperature (4°C) are markedly improved when blending is done at higher temperatures. The usual procedure involves adding the rubber to molten asphalt at normal mixing temperature or higher, depending on the type (since the asphalt by itself can be emulsified, i.e. cationic or anionic asphalt emulsions are produced, for some purposes a cold mixing technique is applied in which the rubber latex would simply mix with the emulsified asphalt). For example, the latex is added at 130 to 150°C so that the aqueous portion of the latex suspension rapidly flashes off and the rubber particles are dispersed through the asphalt. Higher temperatures, i.e., 155 to 180°C, are however used for mixing tire powders and asphalt. By the end of one hour reaction time, the Brookfield viscosity of the rubber modified asphalt should reach a plateau and remain constant during subsequent mixing and or storage with little or no change in viscosity. If the blend can not be used in the desired application within 2-4 hours, the shelf life may be extended several days by lowering the temperature to 150-155°C. Agitation is necessary during this storage period to prevent the rubber from separating from the asphalt. This is a primary indication that this rubbery material is somewhat incompatible with the asphalt. If the viscosity drops during blending or storage, either a catastrophic phase separation is occurring or the asphalt has begun to depolymerize due to overheating.

The mixing operation is the most critical step in the preparation of rubber-asphalt blends. The methods employed seem to influence both the end-product

and benefits gained. The following variations to the usual high temperature mixing procedure have been commonly used (in the US) to incorporate rubber into asphalt cements.

a) Crumb rubber. Early attempts included the mixing of relatively large particles of crumb rubber (8-20 mesh) into the final product. These particles remain as discrete "chunks" of rubber swollen at the surface by the maltenes in the asphalt composition. Aromatic kerosines are added to increase to workability of the asphalt-rubber binder, but at least 20% and often as much as 40-60% more asphalt is required to produce acceptable mixes [11]. The higher cost of these mixes limits their applications to the control of reflective stress cracking.

b) A "dry process" has been evaluated for dispersing larger rubber particles (1/16 to 1/8 inch) directly in the aggregate before the asphalt binder is added. The rubber is added at loadings of 3 - 4% of the aggregate; a special aggregate gradation is required to eliminate possible crumb clumping and premature stripping. The process calls for 1.5-3% more liquid asphalt than conventional hot mix [12]. Sold under the tradename "Plusride" , the mixture has been demonstrated to reduce the harmful effects of road icing and reduce the stopping distance on ice covered roads by 25%.

c) An aggregate coating technique involves the addition of a special reclaimed rubber product to the heated aggregate in the pug mill (hot paving material mixer) before mixing the asphalt. The heat activated rubber additive quickly becomes liquid, thus coating and encapsulating each aggregate particle in a rubberized sheath. The interstitial asphalt in the pavement contains a small proportion of rubber additive, since one prime purpose of the elastomer in this case is to provide better adhesion between asphalt binder and aggregate (stone) surface.

d) Powdered scrap tires produced by a wet grinding process (80-200 mesh) can be employed in a dry process where the fine rubber powder is mixed with the aggregate before the asphalt binder is added. The high surface area of the powder allows rapid equilibration with the asphalt and a stable asphalt cement is

produced. This procedure appears to be the most promising technique for producing rubber asphalt blends, but facilities for grinding tires to fine particles are limited. Rouse Rubber Industries (Vicksburg, Mississippi) is the closest known company engaged in the manufacturing of finely ground rubber and reclaim from scrap tires and other rubber wastes.

## **USE OF OILS AS A CONSISTENCY MODIFIER FOR ASPHALT/RUBBER BLENDS**

A refinery may stock two grades of asphalt, one at each end of the viscosity spectrum of the entire product grade requirements. Intermediate grades are prepared by blending (proportioning) the extremes. The preparation of asphalts in liquid form by blending (cutting back) an asphalt with petroleum distillate fraction is customary. There are three general types of cutback asphalt which differ mainly in the amount and type of the diluent (oil) used [15]. Preparation is accomplished by simple blending of the diluent into the hot base asphalt. The slow-curing type, also called road oil, is made by blending the asphalt with 0-50% gas oil. Medium-curing and rapid-curing asphalts differ mainly in the amount of diluent (15-45% kerosene or naphtha, respectively) and in the kinematic viscosity of the blended product (ranging generally from 70 to 6000 cSt).

The development of SBR (i.e., styrene-butadiene rubber) placed a greater demand on softeners for ease in processing than was the case with natural rubber, and petroleum oils fulfilled this softener function efficiently and inexpensively [16]. It has been common practice to use 5-20 parts of oil as processing aids. The use of the petroleum oils greatly expanded with the adoption of oil extended SBR for use in tire compounds (25-50 parts per 100 parts of rubber). Both extender and processing oils have been classified in ASTM D 2226 by the use of molecular analysis. The highly aromatic oils do not lower the Mooney viscosity in SBR as much as paraffinic oils. At the same time, the tensile strength increases as the aromaticity of the oil increases [16].



Vulcanized crumb rubber from used tires is a mixture of natural (less oil extended) and oil-extended synthetic rubber. Natural rubber is primarily used in the carcass and side walls of passenger radial tires, i.e., in the areas where the hot strength properties, superior building tack and better ply adhesion of natural rubber are used to advantage. Oil-extended natural rubber is used in treads of winter tires because of superior grip on snowy and icy roads. In commercial vehicle tires, the natural rubber content generally increases with the size of the tire. Therefore the oil content of crumb rubber from used tires depends on the ratio between passenger and commercial vehicle tires particulated. When a blend of asphalts and crumb rubber is further extended with oils, it is necessary to know in advance the petroleum oil content of rubber used for blending.

## **RHEOLOGY PRINCIPLES FOR SHRP CHARACTERIZATION OF ASPHALTS**

In dynamic mechanical analysis, DMA, a sinusoidal strain or stress is applied to a sample (Figure 1) and the response is monitored as a function of frequency [13]. In a stress controlled instrument (e.g., the CVS rheometer used in the present investigation) force is transmitted in accordance to the generated sine wave to the specimen, through the probe, by means of the function generator. The strain produced in the sample is detected by a differential transformer and produces a signal that expresses the dynamic viscoelasticity of the sample from the force (stress) and the strain. The shear stress  $\sigma$  and the deformation (strain)  $\gamma$  are related via the shear modulus  $G$  as follows:

$$\sigma = G \gamma \quad (\text{eq 1})$$

The primary response of interest is the complex dynamic shear modulus  $G^*$  at frequency  $\omega$ , i.e.,  $G^*(\omega)$ , expressed in Pa. The shear modulus is often known as the rigidity. As shown in Figure 1, this modulus is given by the ratio between the absolute magnitude of the dynamic shear stress,  $\tau(\omega)$ , Pa, and the absolute magnitude of the applied dynamic shear strain,  $\gamma(\omega)$ , m/m:

$$G^*(\omega) = |\tau(\omega)| / |\gamma(\omega)| \quad (\text{eq. 2})$$

In reporting the results of DMA testing , use is often made of the two other parameters, i. e. the storage and the loss moduli,  $G'(\omega)$  and  $G''(\omega)$ , respectively (eq. 3):

$$G^* = [(G')^2 + (G'')^2]^{1/2} \quad (\text{eq. 3})$$

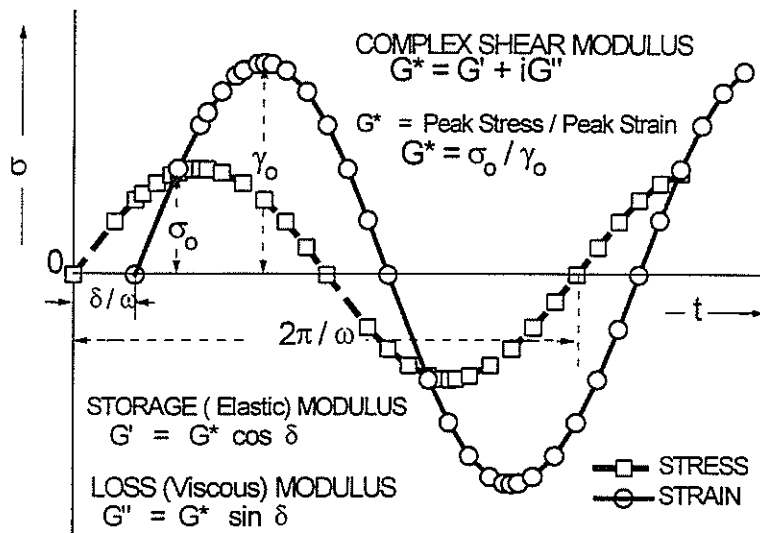


Figure 1. Schematic representation of the stress  $\sigma$  as a function of time  $t$  with dynamic (sinusoidal) loading (strain).

The loss tangent, or tangent of the phase angle,  $\delta$ , which indicates the lag in the response compared to the applied strain or stress, is also customarily used. For purely elastic materials, the phase angle will be zero, whereas for purely viscous materials, the phase angle will be  $90^\circ$ . Thus, the phase angle, expressed as its *sine* or *tangent*, is an important parameter for describing the viscoelastic properties of a paving material. The loss tangent is calculated simply as the tangent of the phase angle, or alternatively, as the ratio of the loss to storage moduli.. Neither polymers nor asphalt cements are ideal energy elastic bodies; they are viscoelastic materials. In such cases the deformation (strain) lags

behind the applied stress (Figure 1). With ideal viscoelastic bodies, the resulting phase angle  $\delta$  in the corresponding vector diagram can be assumed constant, such that the deformation or the strain is

$$\gamma(t) = \gamma_0 \sin(\omega t - \delta) \quad (\text{eq. 4}).$$

Although extensive data can be acquired using dynamic mechanical analysis, selection of the correct parameters in the data analysis for predicting service performance of asphalt binders is not immediately obvious. In analyzing the asphalt cements and the related materials,  $G^*$ , the ratio of the peak stress to the peak strain, reflects the total stiffness. The in-phase component of  $|G^*|$ , i. e. the shear *storage modulus*  $G'$ , represents the part of the input energy which is not lost to heat (the elastic portion). The out-of-phase component of  $|G^*|$ , i. e. the shear *loss modulus*  $G''$ , represents viscous component of it. The complex dynamic shear viscosity  $\eta^*$  can be obtained from  $G^*$  divided by the frequency, while the dynamic viscosity is  $\eta = G'' / \omega$ . Therefore at temperatures at least 20° C above the  $T_g$ , any of these three parameters should relate to flow under load. In the present study  $G^*$  and related components were selected as representative parameters to evaluate the visco-elastic flow of asphalts and blends under investigation. However, it must be recognized that asphalts are complex mixtures and the use of a few simple parameters to evaluate the results may lead to erroneous conclusions. Further, the addition to asphalt of insoluble rubber additives, such as vulcanized rubber particles from used tires, will have a marked influence on the rheology of the blends, but measurements on these blends must be made with care to assure that an accurate assessment of the blend properties is obtained.

## OBJECTIVES AND SCOPE

1. To prepare a series of crumb and powdered rubber blends with AC-10 and AC-30 asphalt cements and assess stability of each blend.
2. To evaluate the potential for using aromatic oils to enhance the compatibility between rubber particles and asphalts.
3. To subject the rubber asphalt blends - with and without aromatic oils - to both TFOT and PAV aging to determine the hardening characteristics and compatibility of the blends during accelerated aging.

Blends of AC10 and AC30 asphalt cements with 15% crumb vulcanized rubber were prepared by adding the rubber to asphalt under vigorous stirring at 220°C and blending @ 170°C for 40 min. Corresponding blends of powdered rubber with 15% to 22.5% rubber were also by adding the rubber to asphalt under vigorous stirring at 170°C and blending at this temperature for 40 min..

A thermally stable aromatic oil was added to the crumb rubber/asphalt blends to enhance the compatibility between asphalts and rubber. The aromatic oil - 5% or 15% of the blend composition - was either co-blended with the rubber and asphalt or the rubber was pre-treated with the oil and subsequently blended with the asphalt.

Dynamic mechanical testing procedures were employed to characterize the asphalt cements and all rubber/asphalt blends. All tank asphalts and blends were subjected to aging by TFOT followed by PAV and recharacterized using SHRP procedures. Low temperature creep response @ -12°C was determined on all samples with bending beam rheometry.

## METHODOLOGY

**Asphalts.** Tank asphalts provided by Louisiana and Arkansas refineries were used for the preparation of rubber/asphalt mixtures. Sample rubber blends were prepared using grades (number of sources) AC-10 (2) and AC-30 (2) as follows: LION AC-10, EAGLE AC-10, MARATHON AC-30 and ERGON AC-30. The high temperature viscosities of each of these asphalts are included in Tables 3-7 and the rheological properties are summarized in Table 8.

**Vulcanized Rubber Particles:** Rubber from ground tires was received from suppliers as crumbs (Granular Products & Services, Inc., Fort Worth, Texas 76117) or fine powder (Rouse Rubber Industries, Inc., Vicksburg, MS). The crumb rubber, CR, had a maximum particle size of ca. 1.0 mm. The powder rubber, PR, was a fine 200 mesh (0.074 mm) ground rubber. The content of extractables (with benzene and methyl-isobutyl ketone) from CR was 15.15%. It is assumed that the extractables are mostly mineral oils used in rubber industry for compounding rubber and black carbon.

**Aromatic Oils:** Three aromatic oils (AOs) from SUN OIL Co. were considered for blending with asphalt and vulcanized rubber from used tires:

Hydrolene 50T (H50T), Hydrolene 90T (H90T) and Hydrolene 600T (H600T). The oils are complex mixtures of hydrocarbons obtained from a solvent extraction process of a heavy paraffin distillate. They consist predominately of aromatic hydrocarbons having carbon numbers mainly in the range of C20 through C50. The chemical properties of each oil are summarized in Table 1. Thermal stabilities (figures 2 and 3) and viscosities (figure 7) of the oils were tested at the temperatures used for blending asphalts and rubbers, i.e., 170°C and 220°C.

**Vulcanized Rubber/Asphalt Binder Blends.** The crumb rubber was used as received from the suppliers. Depending on the amount of the material needed for further investigations, blending was done either in aluminum containers normally used as soft drink cans using a high speed lab stirrer (3,000 rpm) or

TABLE 1  
 PROPERTIES OF AROMATIC OILS

Properties	Hydrolene 50T	Hydrolene 90T	Hydrolene 600T
Ave. Molecular Wt.			
g/mole	347	396	719
Flash Point, °C (°F)	198 (390)	210 (410)	276 (530)
Density, g/cc	0.959	0.9925	0.962
Polar Compounds, wt %	5.2	10.4	15.9
Aromatics, wt %	66.5	73.2	57.9
Saturates, wt %	28.3	16.3	26.2

in larger metallic containers (1/8 Gal. or 1 Gal.) using a high shear laboratory mixer (Silverson L4RT mixer with 6,000 rpm under full load) The cans were maintained at  $T+5^{\circ}\text{C}$ , where T is the mixing temperature. Particular blending protocols were observed as follows. In order to obtain CR/AC blends, i.e., [AC + 15%CR] blends, the crumb rubber was added to AC at  $220^{\circ}\text{C}$ , the temperature was allowed to drop to  $T = 170^{\circ}\text{C}$  and the blending was continued at this temperature for 40 min. When aromatic oil was used, it was mixed with AC under stirring before the temperature reached its maximum at  $220^{\circ}\text{C}$  and CR was added as described above. Direct mixing of all three components is designated as follows: [AC + CR + AO]. In order to prepare blends with CR pre-wetted with AO, e.g., [AC + (15%CR + 15%AO)], equal amounts of CR and AO were blended manually in a can at  $100^{\circ}\text{C}$  and the CR/AO particles was allowed to stay at this temperature for 24 hours. The preswollen rubber particles were then added to the AC at  $220^{\circ}\text{C}$  and the mixing was continued as described above. In order to prepare AC/PR blends, the powder rubber was added to AC

at  $T = 170^{\circ}\text{C}$  and the blend was stirred for 20 min. In all cases the cooling to ambient temperature was not monitored. The cans were also used for the storage of blends.

**Methods.** The *thermal stability* of a given material can be measured by registering the variation of weight versus a linear increment of temperature (i.e., by the thermogravimetric method or thermogravimetry, TG). A Seiko TG/DTA 220 thermobalance calibrated for temperature with indium (m.p.  $256.4^{\circ}\text{C}$ ) was employed to estimate the weight loss @  $170^{\circ}\text{C}$  and  $220^{\circ}\text{C}$  of all ingredients to be blended, i.e., tank asphalts, rubbers and aromatic oils. The TG analysis was conducted on  $\approx 10$  mg samples weighted in an aluminum sample pan using an empty aluminum sample pan with cap as a reference. The thermal analysis (heating) was carried out in nitrogen with a rate of  $5^{\circ}\text{C}/\text{min}$ .

A *Brookfield viscometer* (Spindle # 3) was used to measure the *consistency of aromatic oils* at  $170^{\circ}\text{C}$  and  $220^{\circ}\text{C}$ . The viscosity data at these temperatures of all three aromatic oils considered for blending are compared in figure 7. H50T and H90T are low viscosity aromatic oils even at ambient room temperature ( $\eta @ 20^{\circ}\text{C} < 150$  cP for H50T and  $< 700$ cp for H90T;  $1,000$  cP =  $1$  Pa.s). H600T is a more viscous aromatic oil, i.e.,  $\eta @ 20^{\circ}\text{C} \approx 1,000$  cP. However, H600T is the most thermostable oil as compared to other two AOs, and its viscosity is low at working temperatures used for rubber soaking ( $100^{\circ}\text{C}$ ) and/or blending, e.g.,  $\eta @ 100^{\circ}\text{C} < 150$  cP and  $\eta @ 170^{\circ}\text{C} < 50$  cP. This AO was the only one utilized in the present investigation for blending with rubber and asphalts.

A *Brookfield viscometer* specially designed for asphalt characterization (Spindle # 27 @ 100 rotations per minute, rpm, corresponding to  $1.67\text{Hz}$  or ca.  $10$  rad/s) was used to evaluate the change in *consistency of binders* at high temperatures ( $135^{\circ}\text{C}$ ). All determinations were made @ 100 rpm in order to compare the Brookfield viscosity data with rheological data obtained by extrapolation to  $135^{\circ}\text{C}$ . The viscosity was calculated from the loss modulus

using the relationship  $\eta = G''/2\pi\nu$ , where,  $\nu = 1.5$  Hz. Viscosity variations produced by varying both the amount of rubber and/or oil added and the mixing protocol (i.e., either pre-wetting or simultaneous mixing of AO with rubber particles) were measured.

A Bohlin CVS *dynamic shear rheometer*, DSR, specially designed for characterization of asphalt cements (Bohlin Instruments Div., Metric Group Inc., Cranbury, NJ) was used to investigate the *rheological behavior* of tank asphalts and of their blends with vulcanized PR or CR rubbers or only with CR and aromatic oils. The SHRP protocol [14] was observed for performing the measurements. Correspondingly, the large spindle (25 mm) with the gap set for 1000 microns (1 mm) was used for all samples tested above room temperature.

**Blend Aging.** Representative asphalt and asphalt/rubber blends (both crumb rubber and powder rubber as described above) were selected for RTFO and PAV aging. RTFO bottles loaded with  $35 \pm 0.5$ g material were subjected to aging in the oven at  $163^\circ\text{C}$  for 85 min under an air jet positioned to blow air (flow rate: 4,000 mL/min) into each sample bottle at its lowest travel position while being circulated in the carriage (rotation rate of the carriage:  $15^\circ/\text{min}$ ). Pure asphalt samples were RTFO aged without any difficulties and were submitted to the next aging step in the PAV. Asphalt/rubber blends, especially those containing crumb rubber, foamed excessively. Therefore, the RTFO test was discontinued and replaced with the thin film oven test (TFOT). New samples were prepared ( $50 \pm 0.5$ g material) which were aged in the TFOT oven at  $163^\circ\text{C}$  for 5 hr under a continuous air flow. All samples were weighed before and after the TFOT treatment. A gross phase separation was noted in the case of certain asphalt/crumb rubber blends. RTFO pure asphalt specimens and all TFOT samples ( $50 \pm 0.5$ g each) were subjected to PAV aging at  $100^\circ\text{C}$  and 2070 kPa (300 psi) for 20 hr. Photographs of blends were taken before and after aging in each particular cases (*vide infra*).

**Bending Beam Rheometer Measurements** The bending beam rheometer (Applied Test System, Butler, NC) was used to measure the low-temperature



creep response of PAV aged tank asphalts and rubberized asphalt blends. The SHRP protocol [14] was observed for these measurements. The data, which were collected at six loading times (8, 15, 30, 60, 120 and 240 sec) for a load on the beam of  $100 \pm 5$  g, allowed the calculation of the creep stiffness,  $S(t)$ , and the creep rate of the sample under load,  $m$ , as the absolute value of the slope of the log stiffness versus log time curve. The required calculations were performed by a software program supplied with the rheometer.

## RESULTS AND DISCUSSION

### THERMAL STABILITY OF TANK ASPHALTS, VULCANIZED CRUMB RUBBER FROM USED TIRES AND AROMATIC OILS

Asphalts, rubbers, and aromatic oils, all should be thermally stable at the peak temperatures experienced during the preparation of blends. To assess potential problems that might arise during a mixing process incorporating aromatic oils, the thermal stability of the pure aromatic oil mixtures was examined using thermogravimetric analysis, TGA. The stability of aromatic oils is presented as the weight loss @ 170°C and 220°C in figures 2 and 3, respectively. All AOs were stable @ 170°C, i.e. the loss of material by evaporation and/or decomposition was less than 1% in each particular case. However, a significant evaporation of lighter components was registered at 220°C for both AO H50T (weight loss > 10%) and AO H90T (weight loss > 5%); less than 1% weight was lost at this temperature in the case of AO H600T (figure 2). If the mixing protocol were limited to temperatures up to 170°C, any of the oils could be used effectively. However, to allow us to relate experimental data previously obtained with crumb rubber blends, we chose to continue to mix crumb rubber at 220°C and thus restricted the selection of aromatic oils to AO H600T.

The thermal stability @ 170°C and 220°C of tank asphalts, CR and AO H600T is presented as the percent of initial weight at these temperatures in figures 4 and 5, respectively. The least stable of these components was the crumb rubber which registered a weight loss of almost 1.5% @ 170°C (figure 4) and 3.5% @ 220°C (Figure 5). The loss was due presumably to degradation and/or evaporation of some extractable ingredients from the rubber, perhaps mineral oils (see above). 99.9% of the initial weight of tank asphalt cements was still present @ 170°C (figure 4) but ca. 0.6% of tank Ergon AC-30 was lost @ 220°C, while the tank Lion AC-10 was more stable at this temperature (< 0.2%). The thermal stabilities @ 170°C and 220°C of the four tank asphalts used in this study are presented in Table 2. Ergon AC-30 was the least stable of the four, with a weight loss @ 220°C higher than 1.10%. Eagle AC-10 lost also almost 0.90% at this temperature. These data correlate with the stability of asphalts and blends @ 163°C during aging.

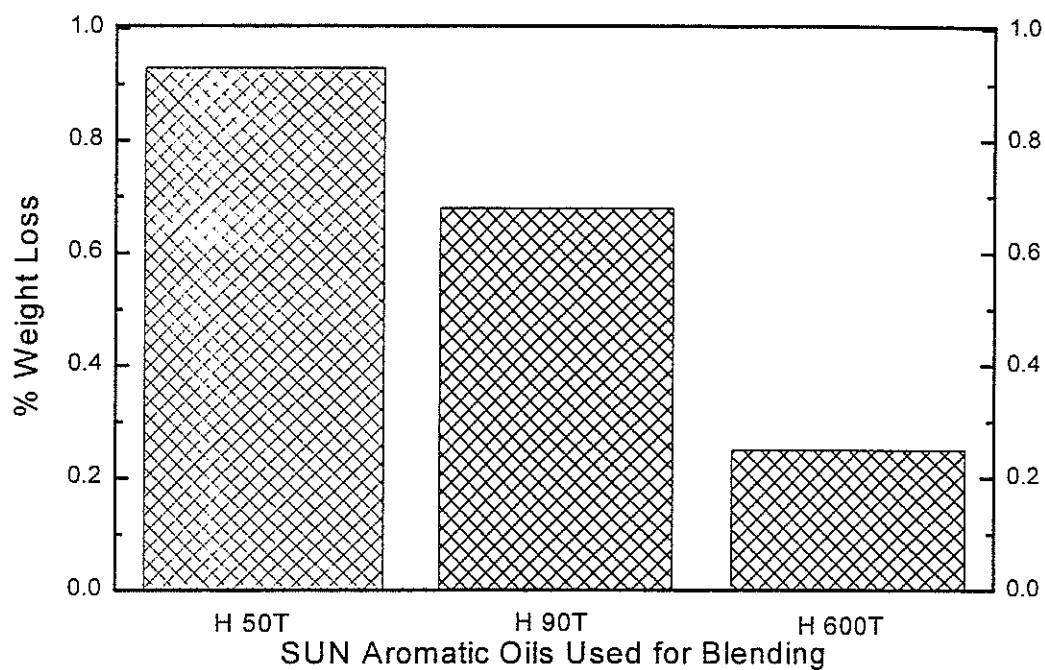


Figure 2. Percent weight loss of aromatic oils at 170°C.

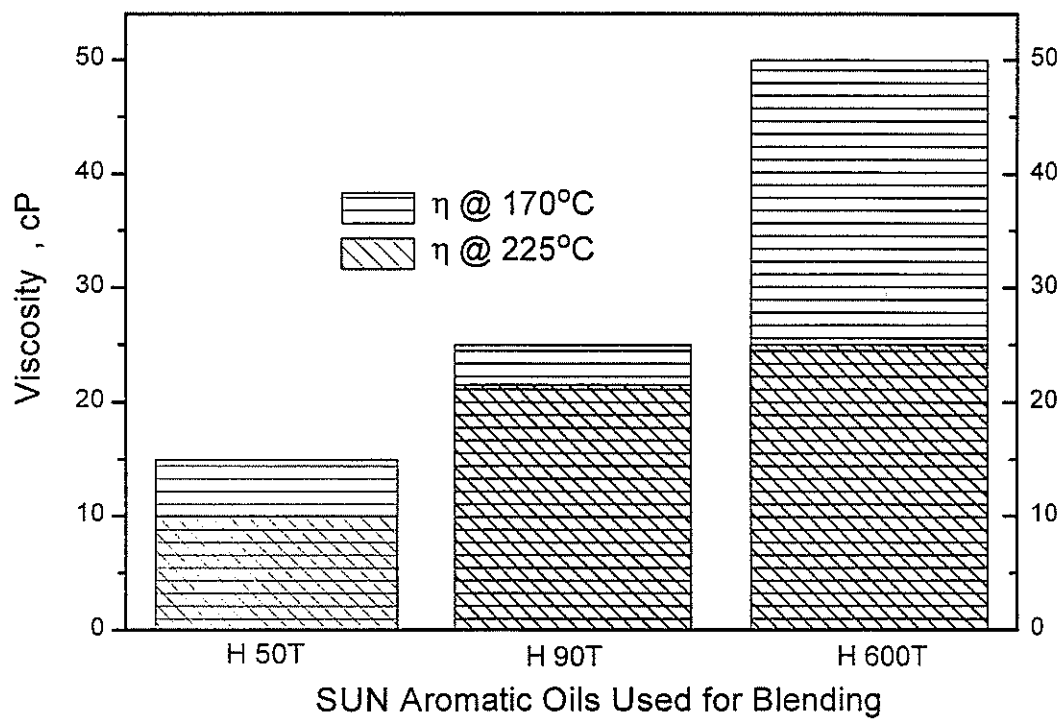


Figure 3. Comparison between percent weight loss of aromatic oils at 170°C and 220°C.

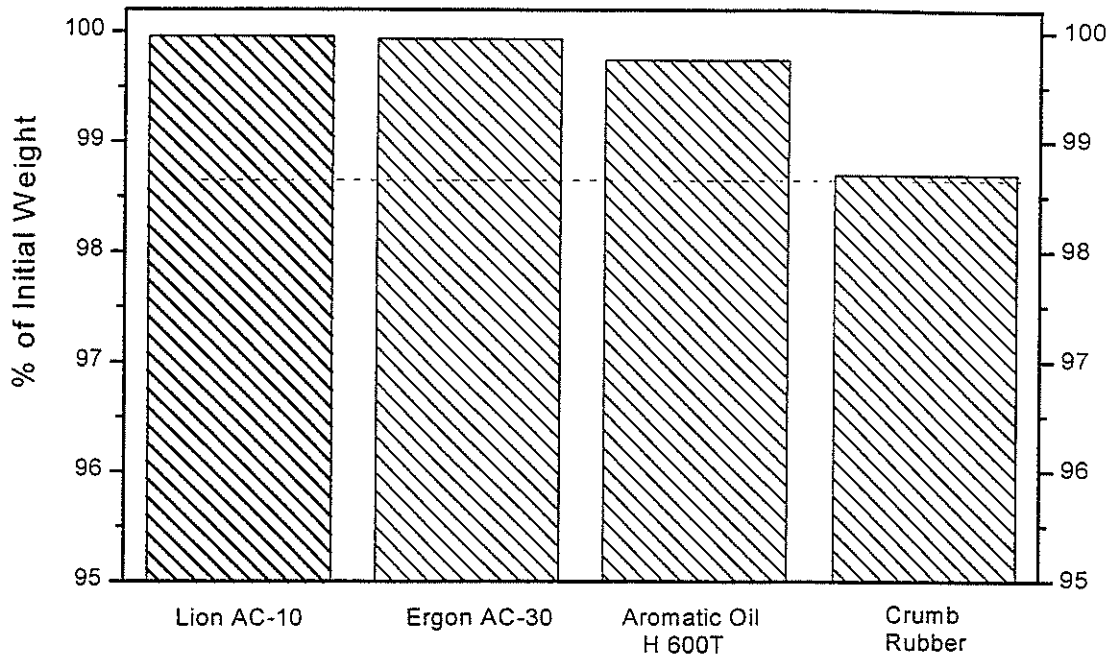


Figure 4. Comparison of residual weight after heating to 170°C of tank asphalts, aromatic oil and crumb rubber employed in this study.

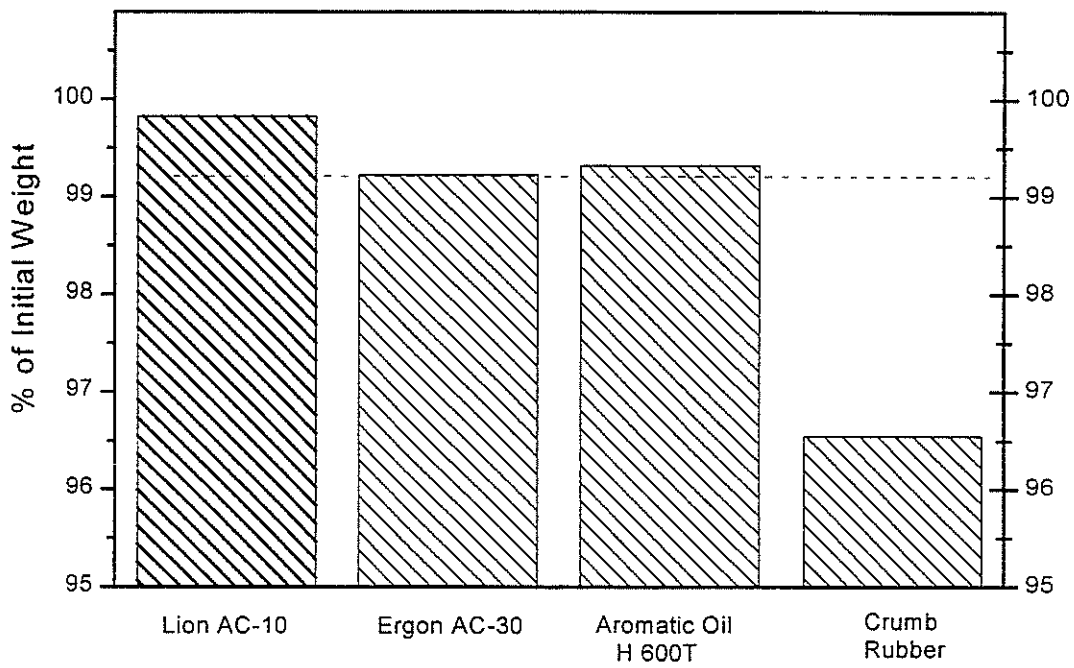


Figure 5. Comparison of residual weight after heating to 170°C of tank asphalts, aromatic oil and crumb rubber employed in this study.

TABLE 2

THERMAL STABILITY OF ASPHALT UTILIZED FOR BLENDING WITH CRUMB RUBBER AND AROMATIC OILS EXPRESSED AS WEIGHT LOSS AT 170°C AND 220°C

<i>Asphalt</i>	<i>Weight Loss @ 170°C</i>	<i>Weight Loss @ 220°C</i>
LION AC-10	0.030%	0.172%
EAGLE AC-10	0.070%	0.887%
ERGON AC-30	0.200%	1.114%
MARATHON AC-30	0.055%	0.770%

### CONSISTENCY OF TANK ASPHALTS, OF AROMATIC OILS, AND OF RUBBERIZED ASPHALT BLENDS CONTAINING VULCANIZED CRUMB RUBBER AND AROMATIC OILS

Polymeric additives usually have higher softening points than tank asphalt cements, thus, the consistency of the base asphalt at higher temperatures is increased. The increase of viscosity as a result of rubber addition depends significantly upon both the nature of the asphalt cement and the dimension of rubber particles. A SHRP specification suggests that the viscosity of asphalt binders at 135°C be less than 3 Pa•s in order to ensure pumpability at the hot mix asphalt plant. Higher viscosity blends may be employed if their workability and pumpability are demonstrated. It has been shown before [2] that AC-10 and AC-20 blends containing 15% crumb rubber could be produced within the 3 Pa•s specification. However, the AC-30 asphalt grades produced blends with 15% CR having the consistency at 135°C - depending on the nature of the tank asphalt - between 2.3 and 7.5 Pa•s, which may not be acceptable. It has been found also [2] that powdered rubber enhanced the viscosity of the mixes more dramatically; values ranging between 4 and 7 Pa•s were recorded for higher rubber concentrations, i. e., ≥15%, for AC10 blends.

TABLE 3  
 VISCOSITY @ 135°C OF TANK LION AC-10 ASPHALT CEMENT AND OF ASSOCIATED  
 BLENDS CONTAINING VULCANIZED POWDER RUBBER

ASPHALT CEMENT OR BLEND	UNAGED $\eta$ (mPa.s)	AFTER TFOT $\eta$ (mPa.s)	AFTER PAV $\eta$ (mPa.s)
AC10	273	442	519
AC+15%PR	2,505*	2,433	2,550*
AC+17.5%PR	7,580**	4,470*	4,280*
AC+22.5%PR	***	***	***

\* Determined @ 50 rpm (out of scale for 100 rpm)

\*\* Determined @ 30 rpm (out of scale for 50 rpm)

\*\*\* Completely separated in swollen rubber and asphalt liquid phases.

**Blends with Powdered Rubber** The consistency at 135°C of rubberized asphalt cements obtained by blending Lion AC-10 with powder rubber is compared in Table 7. The aging procedures had less impact upon a blend containing 15% PR; the viscosity after PAV was only slightly higher (2%) than that of the unaged material. An inspection of the dependence of the DSR (absolute) viscosity upon temperature for Lion AC-10 blends containing 15% PR or 15% CR (Figure 6) shows that the PR blend is stable, keeping its consistency at higher temperatures, while CR blends failed at ca. 75°C, i.e., above this temperature, a phase separation occurred and the instrument read an erroneous constant plateau for viscosity. The extrapolated line shows that a stable CR blend should have exhibited the same decrease in viscosity at higher temperatures as the PR composition (both CR and PR blends behaved similarly at lower temperatures (Figure 7,  $T < 60^\circ\text{C}$ ). The source of this instrumental artifact is unknown, but it is highly unlikely that the actual viscosity of the mixture remained constant throughout the high temperature regime.

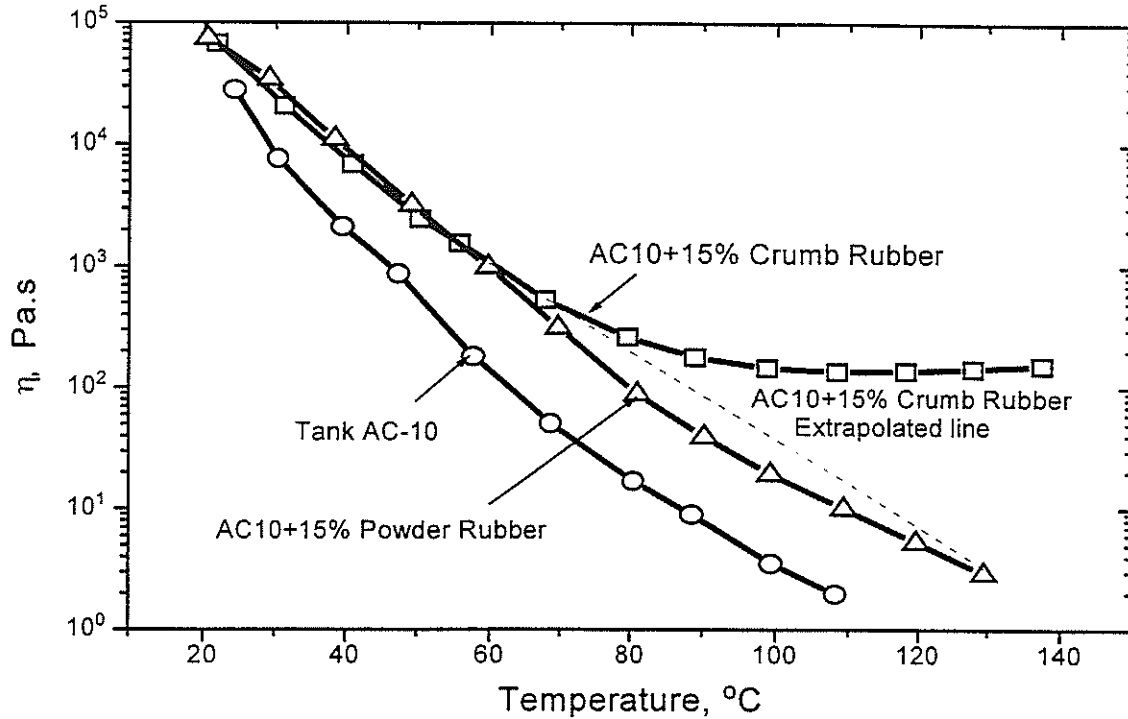


Figure 6. Variation of viscosity with temperature for tank Lion AC-10 binder and the blends containing 15% CR or 15% PR.

The upper concentration limit for making stable blends of powdered rubber with Lion AC-10 was found to be 15 wt%. Additional of 2.5 wt% PR (to 17.5%) produced a very viscous blend @ 135°C which was unstable upon aging (Table 2). After TFOT aging the mix viscosity dropped nearly 50% and continued to decrease after PAV treatment. Attempts to incorporate more PR in the blend failed due to the phase separation during the blending process.

**Blend Compatibility** The problems with blend stability noted in these experiments are indicative of the poor compatibility of simple asphalt rubber blends. The compatibility of vulcanized rubber with asphalt cements depends primarily on:

- 1) the weight ratio of rubber to asphalt cement, i. e., the rubber concentration,
- 2) the nature and the grade of the AC used, i. e., its source and composition, and
- 3) the dimension of rubber particles, i. e., the smaller the particles, the larger the specific surface area and the higher the ability of rubber to absorb the light AC components.

Incompatibility is more apparent in the PAV aged samples, so this should be one of the first tests conducted on asphalt rubber blends. Measuring the viscosity @ 135°C is will determine if the asphalt blend containing vulcanized rubber (or other insoluble polymeric material prone to swell in the asphalt) is phase-separated at higher temperatures before and/or after the aging, i.e., if the blend components are incompatible from the point of view of maintaining the colloidal structure of the asphalt system. Large reductions in viscosity after aging reveal phase separations where the rubber additive is no longer contributing to the viscoelastic properties of the mixture.

Phase separation was also observed in blends of crumb rubber with Lion AC-10 asphalts, i.e., the consistency of AC-10 blends containing 15% CR was decreased by 70% after TFOT aging (Tables 3). Blends of crumb rubber with Eagle AC-10, Marathon AC-30 and Ergon AC-30 (Table 5-6), but the 135°C viscosity of the unaged mixed approach or exceed the suggested SHRP limit of 3 Pa·s. The value of  $\eta$  @ 135°C was brought below the 3 Pa·s limit by presoaking CR with 5% or 10% AO, the blends exhibiting a “normal” behavior after both TFOT and PAV treatments. Thus, premixing aromatic oils with crumb rubber is a technique for consistently producing blends within expected SHRP specifications.

**High Temperature Viscosity** The high temperature viscosities of all three aromatic oils considered for blending are compared in Figure 7. H50T and H90 are low viscosity aromatic oils even at ambient room temperature ( $\eta$  @ 20°C < 150 cP for H50T and < 700 cP for H90; 1,000 cP = 1 Pa·s). H600T is a more viscous aromatic oil,  $\eta$  @ 20°C  $\cong$  1,000 cP., however, H600T is the most thermostable oil as compared to other two AO's. Fortunately, the viscosity of H600T is relatively low at the working temperatures used for rubber soaking (100°C) and/or blending, e.g.,  $\eta$  @ 100°C < 150 cP and  $\eta$  @ 170°C < 50 cP, so this oil was selected for further study.



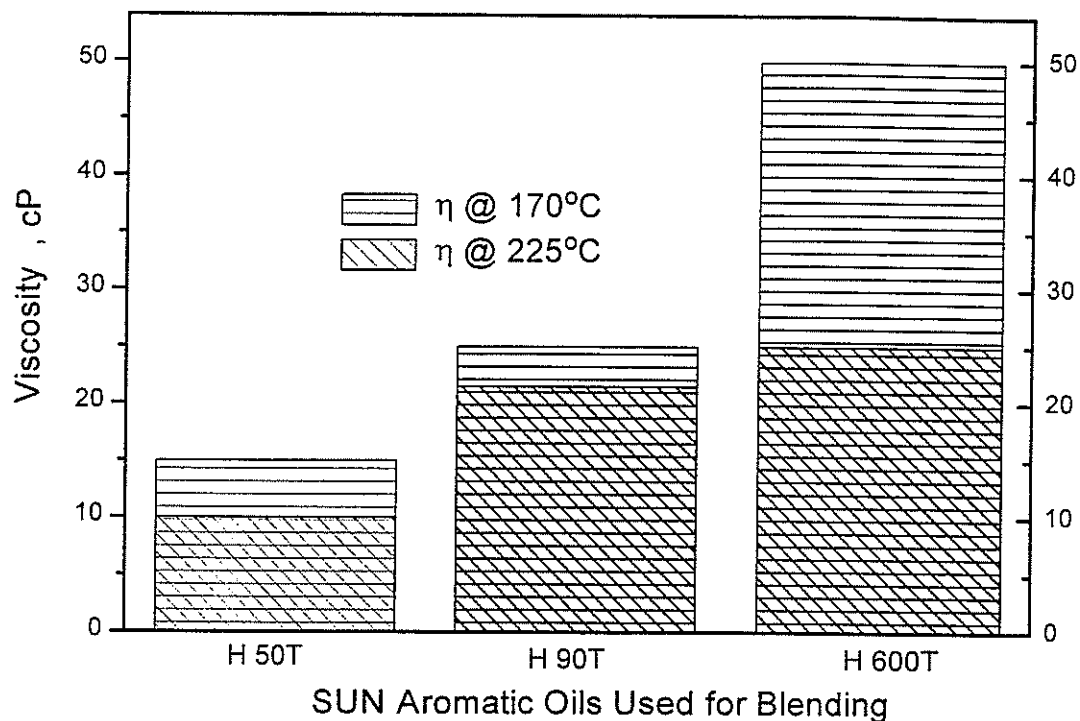


Figure 7. Brookfield viscosity of aromatic oils at 170°C and 220°C (blending temperatures for asphalts with vulcanized powder rubber and crumb rubber from used tires, respectively).

Viscosity data measured on asphalt blends prepared with variations in both the amount of rubber and oil added and the protocol of addition are summarized in Table 3-6. Data is presented for blends subjected to TFOT and PAV aging as well. The main features of these comparisons may be summarized as follows:

- The viscosity of tank asphalts was higher after aging, with increasing values after TFOT and PAV treatments as expected due to oxidation processes.
- Incorporation of 15% crumb rubber, e.g., [AC + 15% CR] produced a multifold increase in the high temperature viscosity of of unaged blends.
- A catastrophic drop in viscosity, indicative of phase separation, was observed in the case of Lion AC-10 blends containing only CR, particularly after the PAV treatment, e.g., [AC + 15%CR] blend, Table 3.

- A drop of viscosity - as compared to  $\eta$  @ 135°C of the tank asphalt - i.e., a “diluting effect”, was experienced for some cements when the aromatic oil (15%) was co-blended with tank asphalt and CR (15%), e.g., the case of unaged [AC + 15%CR + 15%AO] blends, Tables 3 and 5.
- A consistency @ 135°C lower than that of the tank asphalt was also observed for the co-blended mixtures after TFOT aging in the case of Lion AC-10 (Table 3) and after PAV treatment in the case of Eagle AC-10 and Marathon AC-30 (Tables 4 and 5, respectively).
- A “normal” trend for viscosity was observed after aging for all blends made with CR pre-wetted with aromatic oil, e.g., [AC + (15%CR + 15% AO)] blends. No dilution effect was detected in the unaged blends and viscosity increases were observed after each aging process.
- As expected,  $\eta$  @ 135°C of blends containing 5% AO was higher in all circumstances than that of blends with 15% AO - if the CR was presoaked in AO.

The viscosity data show the importance of selecting the proper protocol for adding aromatic oils to rubber asphalt blends. If the rubber particles are presoaked with the oil, compatible blends with asphalt can be produced. In contrast, direct addition of an aromatic oil to a mixture of asphalt and rubber particles (co-blending) tends to disrupt the integrity of the mix and phase separation occurs, either immediately or after aging.

TABLE 4  
 VISCOSITY @ 135°C OF TANK LION AC-10 ASPHALT CEMENT AND OF ASSOCIATED  
 BLENDS CONTAINING VULCANIZED CRUMB RUBBER AND H600T AROMATIC OIL

ASPHALT CEMENT OR BLEND	UNAGED $\eta$ (mPa•s)	AFTER TFOT $\eta$ (mPa•s)	AFTER PAV $\eta$ (mPa•s)
AC10	273	442	519
AC+15%CR	1,997	470	183
AC+15%CR+15%AO	244	193	862
AC+(15%CR+15%AO)	922	925	1,044
AC+(15%CR + 5%AO)	1,290	1,081	1,645

TABLE 5  
 VISCOSITY @ 135°C OF TANK EAGLE AC-10 ASPHALT CEMENT AND OF  
 ASSOCIATED BLENDS CONTAINING VULCANIZED CRUMB RUBBER AND H600T  
 AROMATIC OIL

Asphalt Cement or Blend	Unaged $\eta$ (mPa•s)	After TFOT $\eta$ (mPa•s)	After PAV $\eta$ (mPa•s)
AC10	200*	475*	695*
AC+15%CR	2,850	3,847	4,570
AC+15%CR+15%AO	445	740	490
AC+(15%CR+15%AO)	751	1,224	1,550
AC+(15%CR + 5%AO)	1,536	1,843	2,138

\* Determined @ 50 rpm

TABLE 6  
 VISCOSITY @ 135°C OF TANK MARATHON AC-30 ASPHALT CEMENT AND OF  
 ASSOCIATED BLENDS CONTAINING VULCANIZED CRUMB RUBBER AND H600T  
 AROMATIC OIL

ASPHALT CEMENT OR BLEND	UNAGED $\eta$ (mPa·s)	AFTER TFOT $\eta$ (mPa·s)	AFTER PAV $\eta$ (mPa·s)
AC30	400*	775	1,141
AC+15%CR	3,177*	3,767*	5,915*
AC+15%CR+15%AO	148	1,701	831
AC+(15%CR+15%AO)	644	1,083	1,606
AC+(15%CR + 5%AO)	1,306	1,682	2,325

\* Determined @ 50 rpm (out of scale for 100 rpm)

TABLE 7  
 VISCOSITY @ 135°C OF TANK ERGON AC-30 ASPHALT CEMENT AND OF  
 ASSOCIATED BLENDS CONTAINING VULCANIZED CRUMB RUBBER AND H600T  
 AROMATIC OIL

ASPHALT CEMENT OR BLEND	UNAGED $\eta$ (mPa·s)	AFTER TFOT $\eta$ (mPa·s)	AFTER PAV $\eta$ (mPa·s)
AC30	345*	625	803
AC+15%CR	2,390**	2,600*	4,250*
AC+15%CR+15%AO	1,880	771	984
AC+(15%CR+15%AO)	1,275	2,255*	2,825*
AC+(15%CR + 5%AO)	1,323	1,992	2,230*

\* Determined @ 50 rpm (out of scale for 100 rpm)

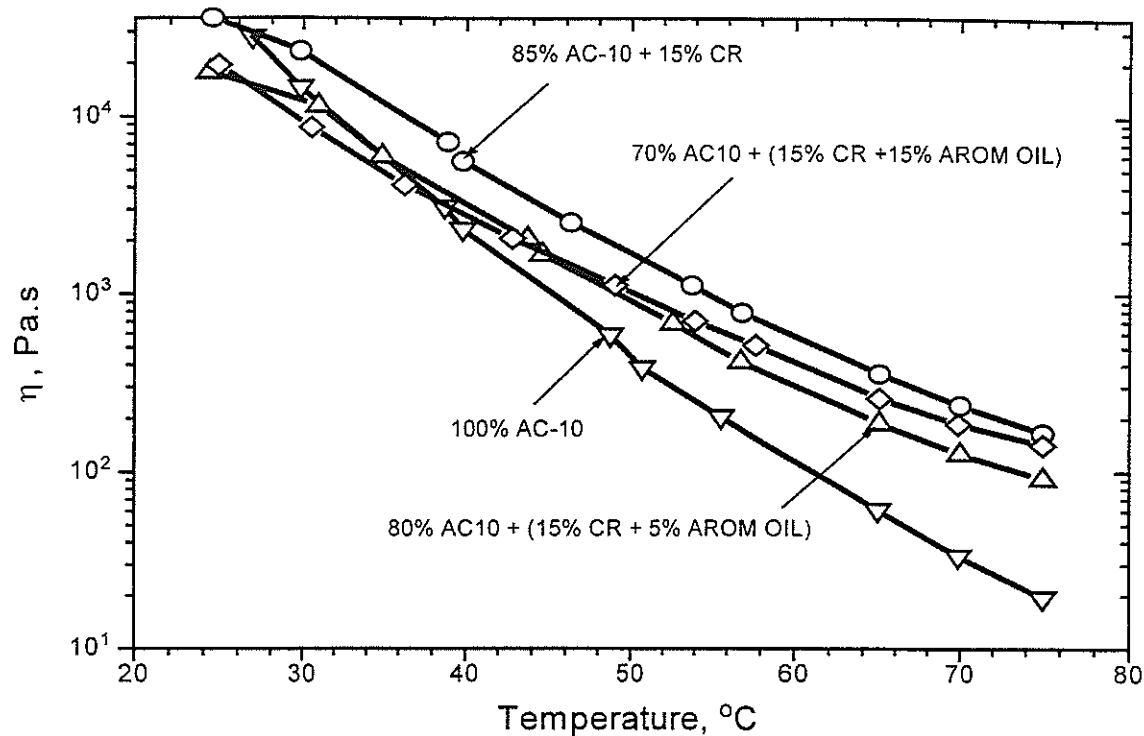


Figure 8. Variation of viscosity at lower temperatures for tank Lion AC-10 binder and the blends containing 15% CR and H600T AO.

## RHEOLOGICAL EVALUATION OF BLENDS

In SHRP specifications, the contribution of the asphalt binder to permanent deformation of asphalt mixes is considered in terms of a minimum value for the stiffness parameter,  $G^*/\sin \delta$ , (i. e., 1000 Pa @ 10 rad/s) at a maximum pavement design temperature [6]. This parameter correlates to that portion of the accumulated, non-recoverable deformation occurring in a pavement that is attributable to the asphalt binder. The higher the value, the less deformable is the pavement. Isochronal plots of  $G^*/\sin \delta$  reveal distinct differences in the contribution of the additives to the blend stiffness.

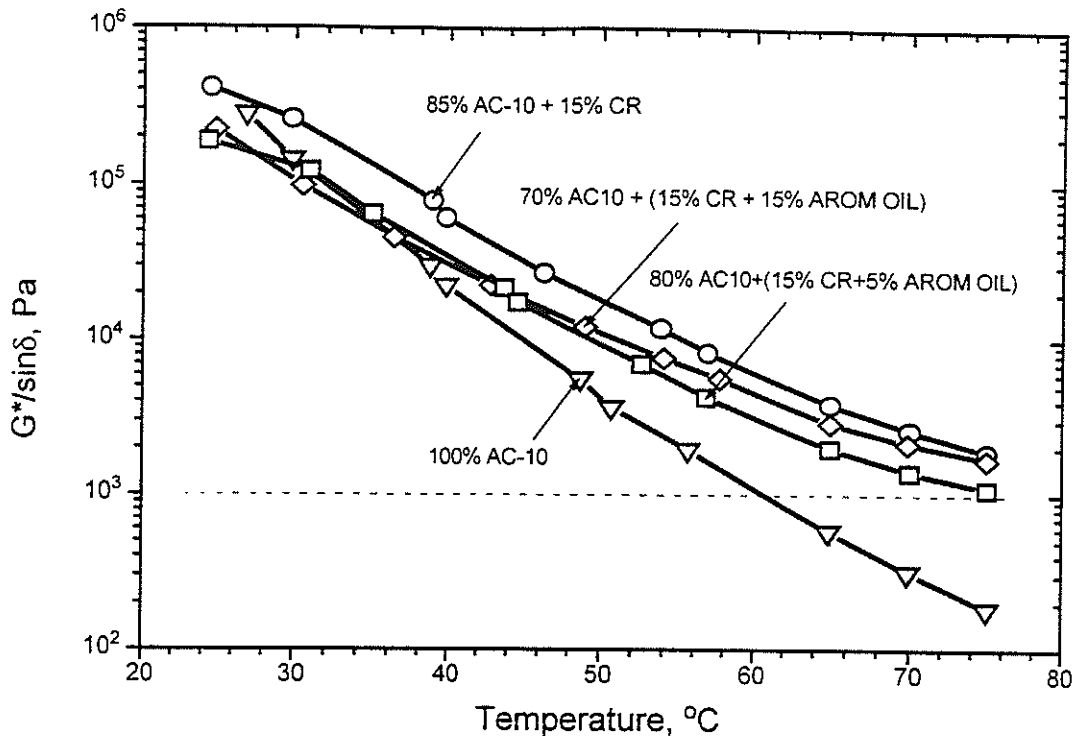


Figure 9. Variation of SHRP stiffness parameter  $G^*/\sin\delta$  with temperature for tank Lion AC-10 binder and the blends with CR and H600T AO.

**SHRP stiffness parameter  $G^*/\sin\delta$**  Figure 9 illustrates the variation of SHRP stiffness parameter  $G^*/\sin\delta$  with temperature for tank Lion AC-10 binder and the blends with 15% CR and 5% or 15% H600T aromatic oil. Based upon this data, the base asphalt would qualify for a maximum use temperature of 58°C; addition of 15% crumb rubber raises the qualification to > 70°C. Since - as viscosity studies have shown - this particular blend phase-separated during aging. Presoaking the rubber with an aromatic oil was used to improve the mixture compatibility. Although addition of the oil made a significant change in the low temperature properties of the mixture (see bending beam data), both 5% and 15% AO containing blends retained a  $G^*/\sin\delta$  above the 1,000 Pa SHRP limit @ 70°C. Thus, presoaking the particles did not reduce the contribution of the additives to the high temperature stiffness.

The protocol for blending the aromatic oil with CR and tank asphalt is a critical variable in producing mixtures with optimum properties, both for the consistency of the

blend and for the rheological characteristics. Viscosity measurements showed a diluting effect when the aromatic oil was added to the tank asphalt and then the mixture co-blended with crumb rubber (e.g., Table 3). This diluting effect is reflected also in the isochronal (1.5 Hz) plots of  $G^*/\sin\delta$  versus temperature for two blends containing 15% CR and 15% AO. The difference in the mode of AO addition to the system is apparent in Figure 10. A blend containing CR presoaked in AO (*Rubber & Oil Preblended curve*) maintained its consistency and exhibited a linear decrease of  $G^*/\sin\delta$  above 50°C. The sample obtained by blending the tank asphalt with CR and AO (*Co-blended curve*) lost its consistency above 50°C and exhibited irrational behavior, (i.e., the stiffness started to increase with temperature). In fact,  $\sin\delta$  is not approaching unity as one would expect when a mixture nears the softening point and becomes a free flowing liquid. Instead the  $\sin\delta$  is decreasing as temperature increases suggesting that the mixture becomes more viscoelastic, when the asphalt component of the binder liquefies. A possible explanation for this behavior is an increased swelling of the rubber particles by the liquid asphalt, but no evidence for that phenomena has been obtained to date. The abnormal behavior of the  $\sin\delta$  suggests that it is not wise to rely on the ratio of  $G^*/\sin\delta$  to predict stiffness properties of rubber asphalt blends without checking the temperature dependence of  $\sin\delta$ .

**Variations in  $\sin\delta$**  The values of the stiffness parameter,  $G^*/\sin\delta$ , of loss and storage moduli, and of the phase expressed as  $\sin\delta$  (read at 70°C from isochronal plots at 1.5 Hz versus temperature) are listed in Tables 7 for neat asphalt cements and some blends prepared from one AC-10 and one AC-30 with crumb rubber. First, it is important to note in Table 8 that none of the neat asphalt cements qualified for a PG-70°C performance grade. The two AC-10 asphalt cements considered in the present investigation qualified for a PG-58°C binder while the AC-30 tank asphalts qualified for PG-64°C. On the contrary, all compositions containing 15% CR (presoaked or not with 5-15% AO) exhibited  $G^*/\sin\delta$  values @ 70°C > 1,000 Pa. Second, all tank asphalt cements exhibited a Newtonian behavior at 70° C, i.e. the storage modulus vanished (or it had an insignificant low value) since at  $\sin\delta \cong 1.0$  it follows that  $G^*/\sin\delta \cong G''$ . In contrast,  $G^*/\sin\delta$  did not correspond with  $G''$  for the measurements made on crumb rubber modified samples because  $\sin\delta < 1.0$  at

any temperature considered. The lower the value of  $\sin \delta$ , the larger the storage modulus, showing that the blend maintained a significant elastic character (Table 9). The variation of  $\sin \delta$  with temperature for tank Lion AC-10 is presented in Figure 11. It is obvious that aging affected the low temperature properties of the cement but above 60°C but unaged and aged samples had  $\sin \delta \cong 1.0$  (a Newtonian flow behavior).

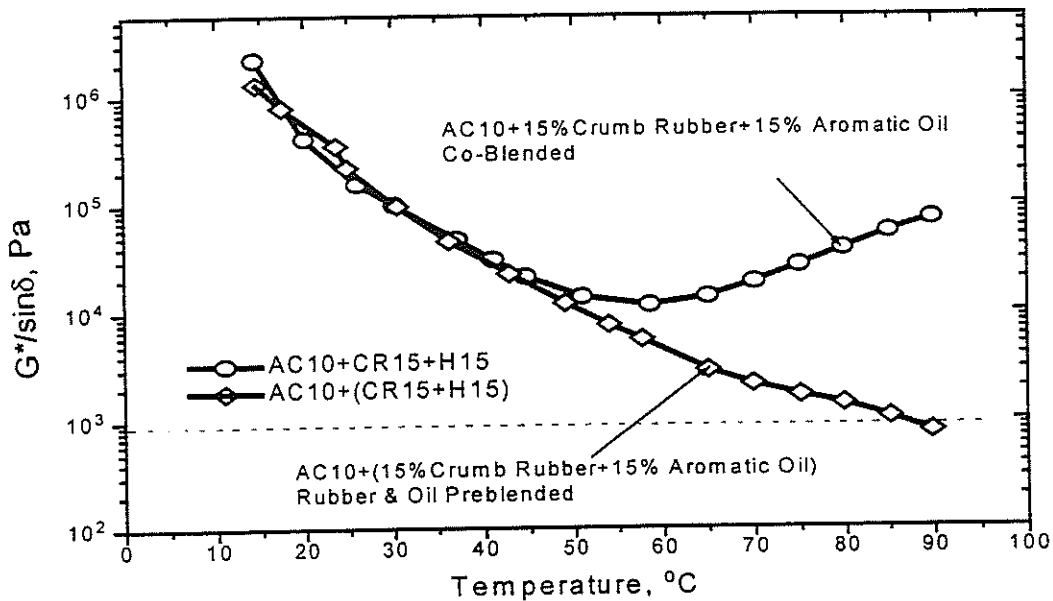


Figure 10. Variation of  $G^*/\sin \delta$  with temperature for blends of Lion AC-10 containing 15% crumb rubber and 15% SUN H 600T aromatic oil preblended or co-blended with the rubber.

TABLE 8  
RHEOLOGICAL PARAMETERS @ 70°C FOR TANK ASPHALTS

ASPHALT BINDER	$G^*/\sin \delta$ (Pa)	$\sin \delta$	$G''$ (Pa)	$G'$ (Pa)
Lion AC-10	316	0.9997	316	8
Eagle AC-10	345	0.9993	344	13
Ergon AC-30	626	0.9984	625	35
Marathon AC-30	786	0.9985	784	36



TABLE 9  
RHEOLOGICAL PARAMETERS @ 70°C FOR BLENDS CONTAINING  
CRUMB RUBBER AND AROMATIC OIL

ASPHALT BINDER	$G^*/\sin\delta$ (Pa)	$\sin\delta$	$G''$ (PA)	$G'$ (PA)
Lion AC-30 + 15%CR	2587	0.8657	1939	1121
Lion AC-10+ (15%CR+15%AO)	2128	0.8290	1463	987
Ergon AC-30 + (15%CR+15%AO)	5724	0.8742	4376	2430

In contrast,  $\sin\delta$  of CR containing asphalt samples never approaches 1.0. As shown in Figure 12 when Lion AC-10 was blended with 15% CR,  $\sin\delta$  of all samples reached a maximum plateau at  $\cong 0.9$  around 60°C. Above this temperature the  $\sin\delta$  of the unaged blend started to decrease. Aging did not affect the high temperature behavior of  $\sin\delta$  but the low temperature profiles of curves for CR containing samples followed the same trend observed for the tank asphalt, i.e.,  $\sin\delta_{PAV} > \sin\delta_{TFOT} > \sin\delta_{UNAGED}$ .

Addition of aromatic oil changed this trend, but the results were dependent on the way the oil was added (Figure 13). As expected from the viscosity data, the *co-blended* sample, in which the CR was not presoaked in AO, behave very poorly, a drastic decrease of  $\sin\delta$  above 40°C was observed. TFOT and unaged samples in which the rubber was preblended with AO had a much better profile for the phase at higher temperatures, but the PAV curve was indicative of a marked non-Newtonian character of the flow after aging. The decrease in  $\sin\delta$  at high temperatures was not related to a phase separation because viscosity measurements at the corresponding temperatures showed that the blend was still very consistent (Table 3).

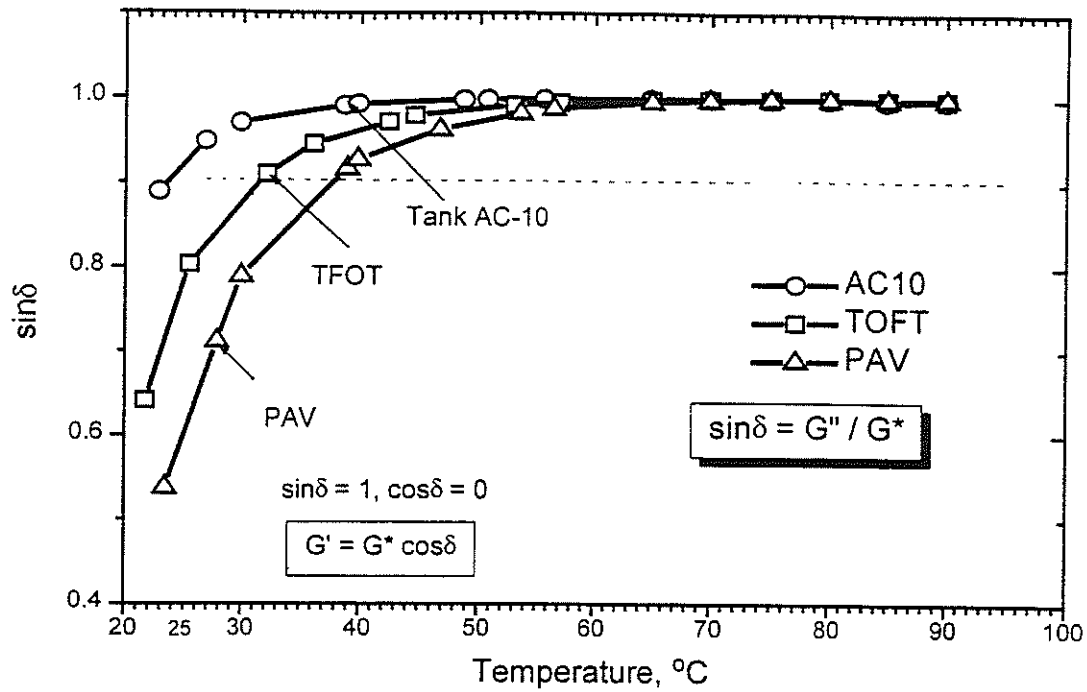


Figure 11. Variation of  $\sin\delta$  with temperature and aging for Lion AC-10 binder.

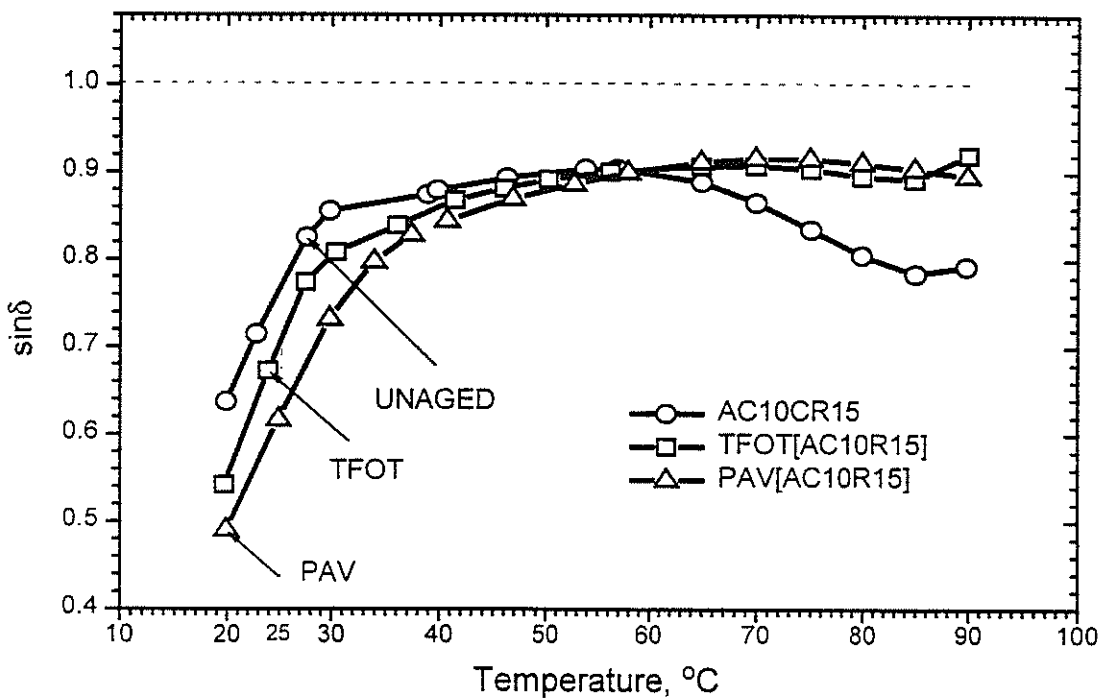


Figure 12. Effect of aging on the variation of  $\sin\delta$  with temperature for Lion AC-10 blended with 15% crumb rubber.

The magnitude of the plateau value of  $\sin\delta$  was dependent upon the aromatic oil content. The highest value was observed for a sample containing 5% AO preblended with CR, but  $\sin\delta$  started to decrease above 60°C (Figure 14). At 70°C  $\sin\delta$  of this blend had

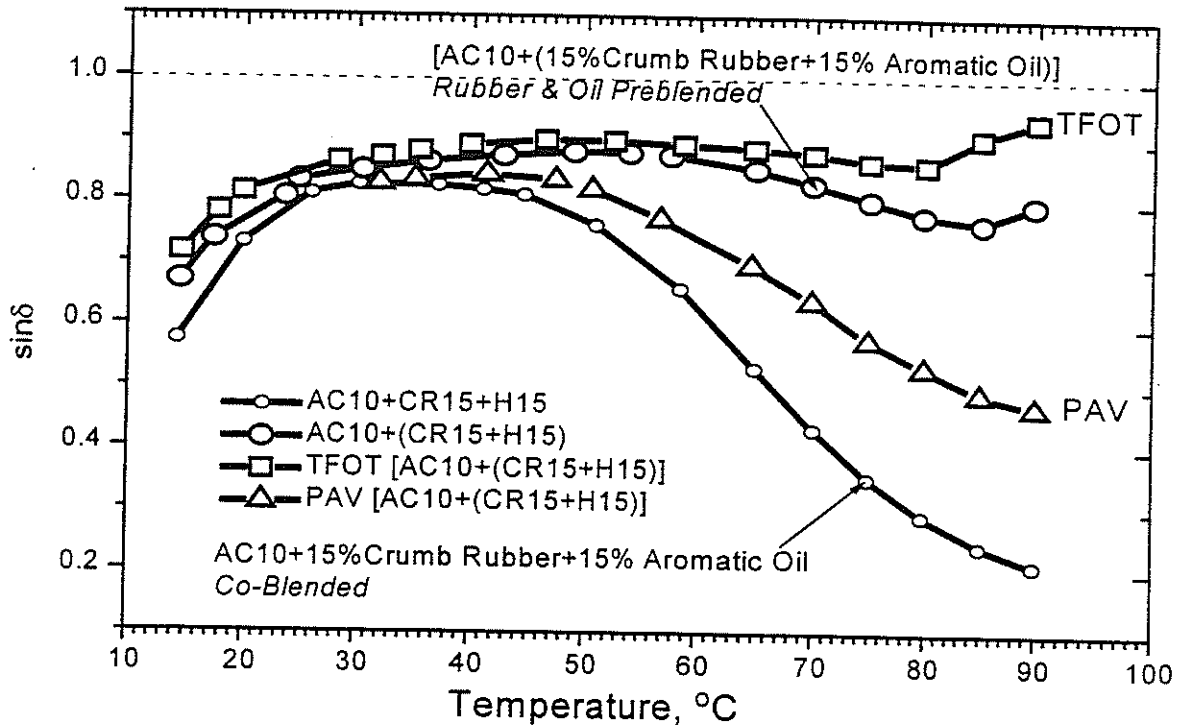


Figure 13. Variation of  $\sin\delta$  with temperature and aging for blends of Lion AC-10 containing 15% crumb rubber and 15% SUN H 600T aromatic oil preblended or co-blended with the rubber.

the same value as that of the blend containing only CR and @ 75°C it was already equal with that of the sample containing 15% AO. Brookfield viscosity, however, was again indicative of a consistent material at higher temperature (Table 3). A similar curve with a decreasing but flatter maximum was observed for a blend containing 15% AO.

A plateau for  $\sin\delta$  was registered for AC30 blends containing 15% CR between 40 and 70°C, and at lower temperatures  $\sin\delta$  of rubberized blends had the same trend as that of the PAV aged base asphalt (Ergon AC-30, Figure 15). The plateau for the PAV aged blend was extended to ca. 80°C, but after that  $\sin\delta$  started to decrease. The plot of the

SHRP stiffness parameter versus temperature for the same samples showed, however, a normal linear decrease for all but the unaged rubberized blend (Figure 16). The consistency of all samples at 135°C was also very high for all samples (except for the base asphalt, Table 5), showing that the decrease of  $\sin\delta$  is not necessarily related directly to a phase separation.

The dimensions of rubber particles are a decisive factor for rheological properties of rubberized asphalts. The smaller the particle, the larger the unitary surface area (e.g., in  $\text{m}^2/\text{g}$ ) and the better the interaction with the asphalt. For the same content of vulcanized rubber from used tires, better results were obtained for blends containing PR as compared with CR containing binders [2]. As seen in Figure 17, the  $\sin\delta$  of the 15% PR blend is going asymptotically to 1.0 - in a similar way as the tank asphalt does - and @ 70°C it is already  $> 0.99$  (at this temperature  $\sin\delta^{\text{Tank AC10}} \cong 1.0$ , while  $\sin\delta^{\text{AC10CR15}} < 0.90$ ). At the same time, the consistency of the base tank asphalt at higher temperatures was very low ( $\eta @ 135^\circ\text{C} = 0.27 \text{ Pa}\cdot\text{s}$ ), while the consistency of PR blend was close to the admissible limit ( $\eta @ 135^\circ\text{C} = 2.50 \text{ Pa}\cdot\text{s}$ ). The consistency of the CR blend was also high ( $\eta @ 135^\circ\text{C} \cong 2.00 \text{ Pa}\cdot\text{s}$ ). Similar results were obtained in a more detailed rheological investigation of PR blends [2].

As one might expect, vulcanized rubber can also improve elasticity (increase the storage modulus) of the asphalt binder and strengthen the asphalt - aggregate bond at high temperatures. Addition of 5% rubber is sufficient to produce markedly enhanced properties without raising the high temperature viscosity excessively. Depending upon the source of the asphalt, addition of 15-20% rubber can produce very stiff mixes. Since a swelling reaction takes place when the asphalt cements are mixed with vulcanized rubber, the degree of the interaction - and therefore the storage modulus of the blend - is mainly dependent upon the chemical composition of the AC and less on its grade.

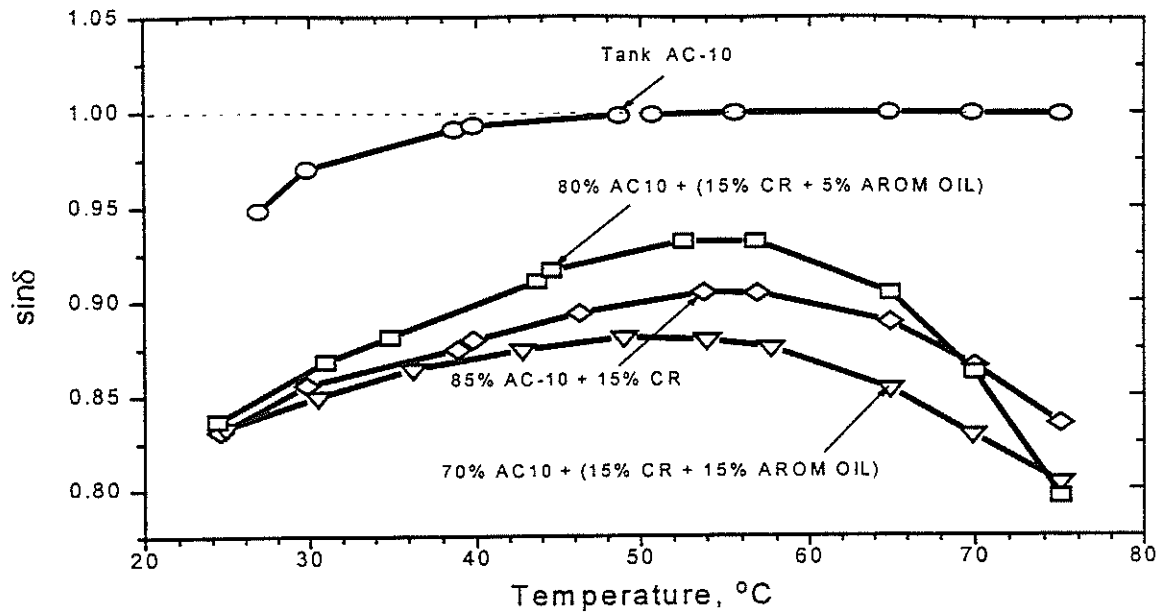


Figure 14. Variation of  $\sin\delta$  with temperature for blends of Lion AC-10 containing 15% crumb rubber and H 600T aromatic oil preblended with the rubber.

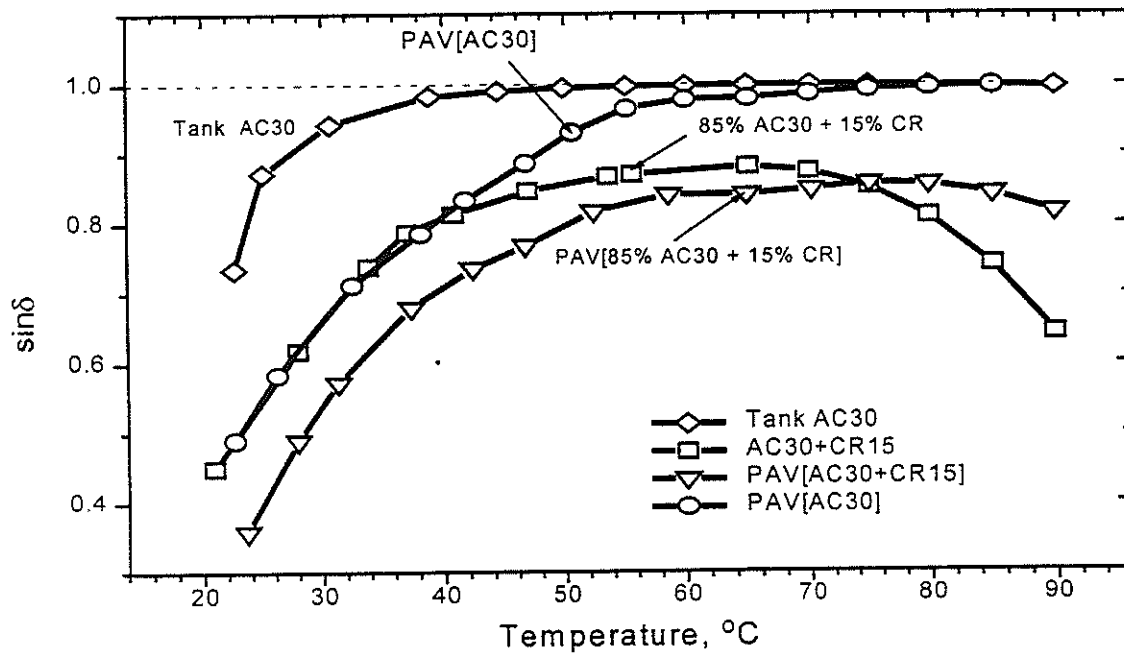


Figure 15. Variation of  $\sin\delta$  with temperature and aging for tank Lion AC-10 and blends containing 15% crumb rubber.

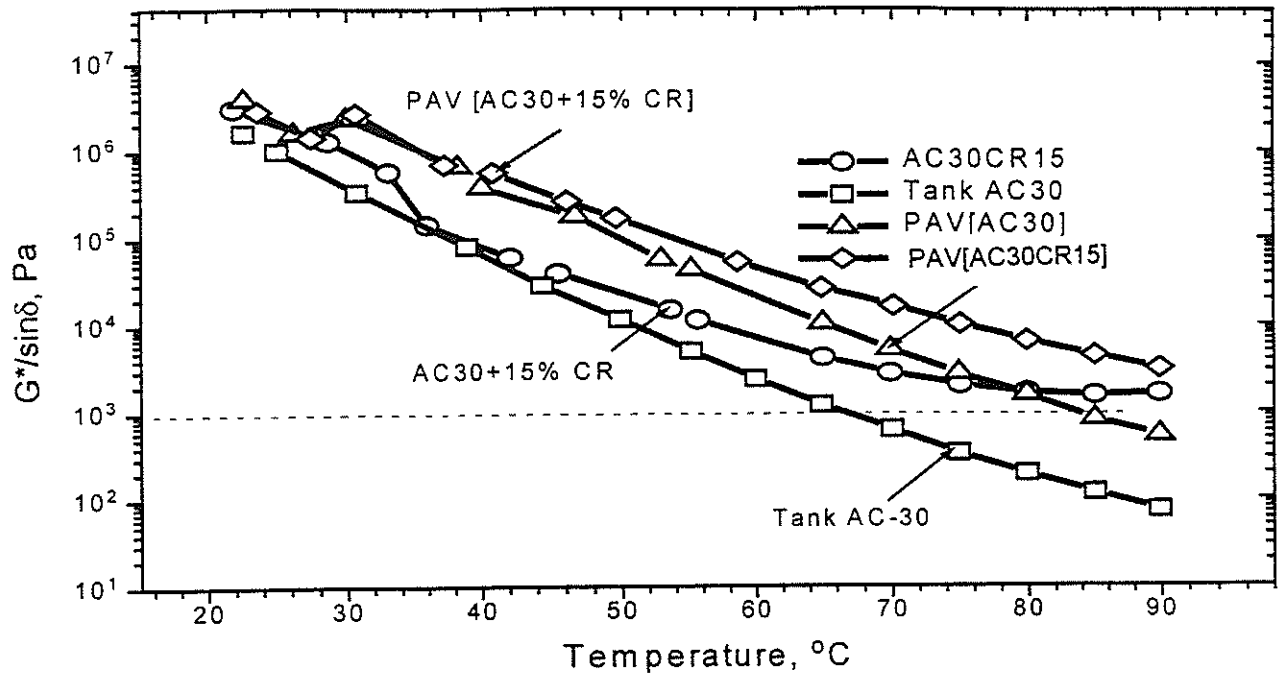


Figure 16. Variation of  $G^*/\sin\delta$  with temperature and aging for tank Ergon AC 30 and blends containing 15% crumb rubber.

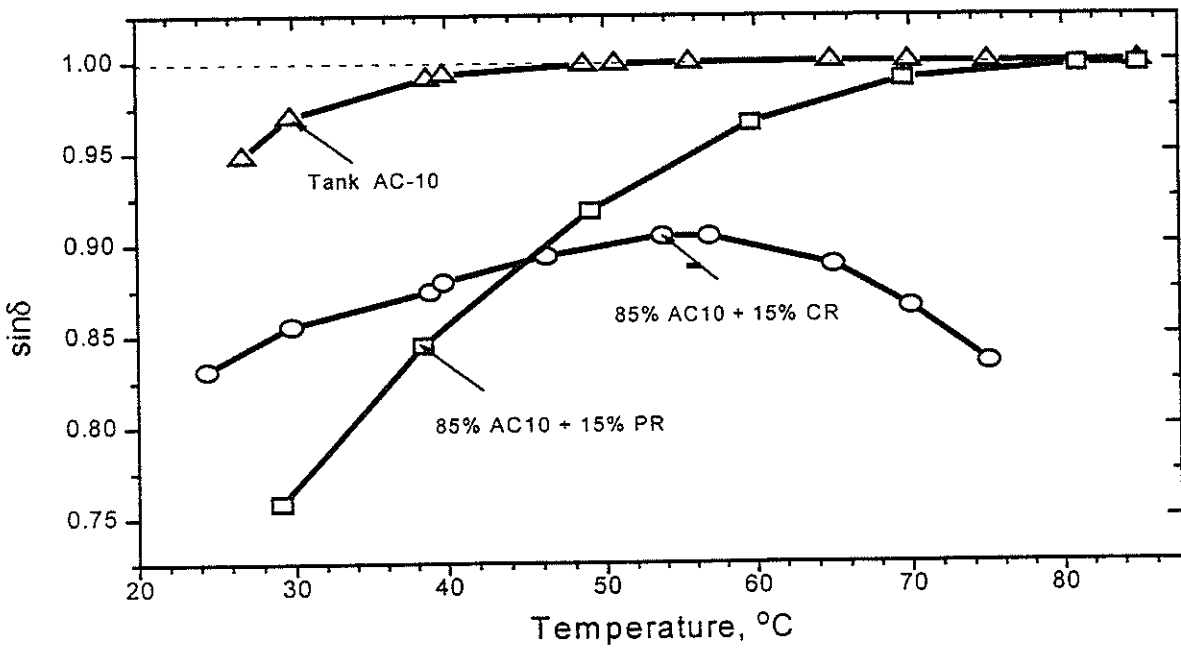


Figure 17. Variation of  $\sin\delta$  with temperature for Lion AC-10 blends containing 15% crumb rubber or 15% powder rubber.

## TFOT AND PAV DATA FOR ASPHALTS AND BLENDS WITH CRUMB AND AROMATIC OIL

Because the RTFO (or TFOT) and PAV protocols are considered aging techniques, no test results are reported, with the exception of mass loss after RTFO (TFOT) aging. Mass loss is reported as the average of the two samples calculated by the following formula [14]:

$$\text{Mass Loss, \%} = [(\text{Original mass} - \text{Aged mass}) / \text{Original mass}] \times 100 \quad (\text{eq. 5})$$

SHRP specifications allow no more than one percent mass loss for all binder grades. Table 10 presents the results after TFO aging of Lion AC-10 and the blends made with vulcanized rubber and aromatic oil. Practically no weight change was registered. No mass loss was observed after TFO aging of the other three asphalt cements (i.e., Eagle AC-10, Ergon AC-30 and Marathon AC-30) and of their blends.

TABLE 10  
TFOT DATA FOR LION AC-10 AND BLENDS WITH CR AND AO

Asphalt Cement or Blend	Original Mass (g)	Aged Mass (g)	Mass Change (%)
Tank AC10	50.01	50.12	+0.22
AC10+15PR	50.12	50.30	+ 0.36
AC10+15CR	50.05	50.14	+ 0.18
AC10+15CR+15%AO	50.04	50.12	+ 0.16

During TFO aging, however, because of the low consistency of the blend at the test temperature (163°C), CR particles “migrated” inertially backward due to the rotation of the carriage, and a gross phase-separation was observed after the test. Figure 18A shows this phase separation for a blend of Ergon AC-10 with 15%CR. A separation of asphalt from swelled rubber might be seen in blends with PR as the rubber content increased from 15% (Figure 18B) to 17.5% (Figure 18C) and, finally to 22.5% (Figure 18D) when a clear

"bleeding" occurred. The PR blends were obtained with Lion AC-10. Additional blending with aromatic oil did not seem to alleviate or moderate this phase separation, irrespective of the asphalt type, i.e., Ergon AC30 (Figure 18E) or Lion AC-10 (Figure 18F)

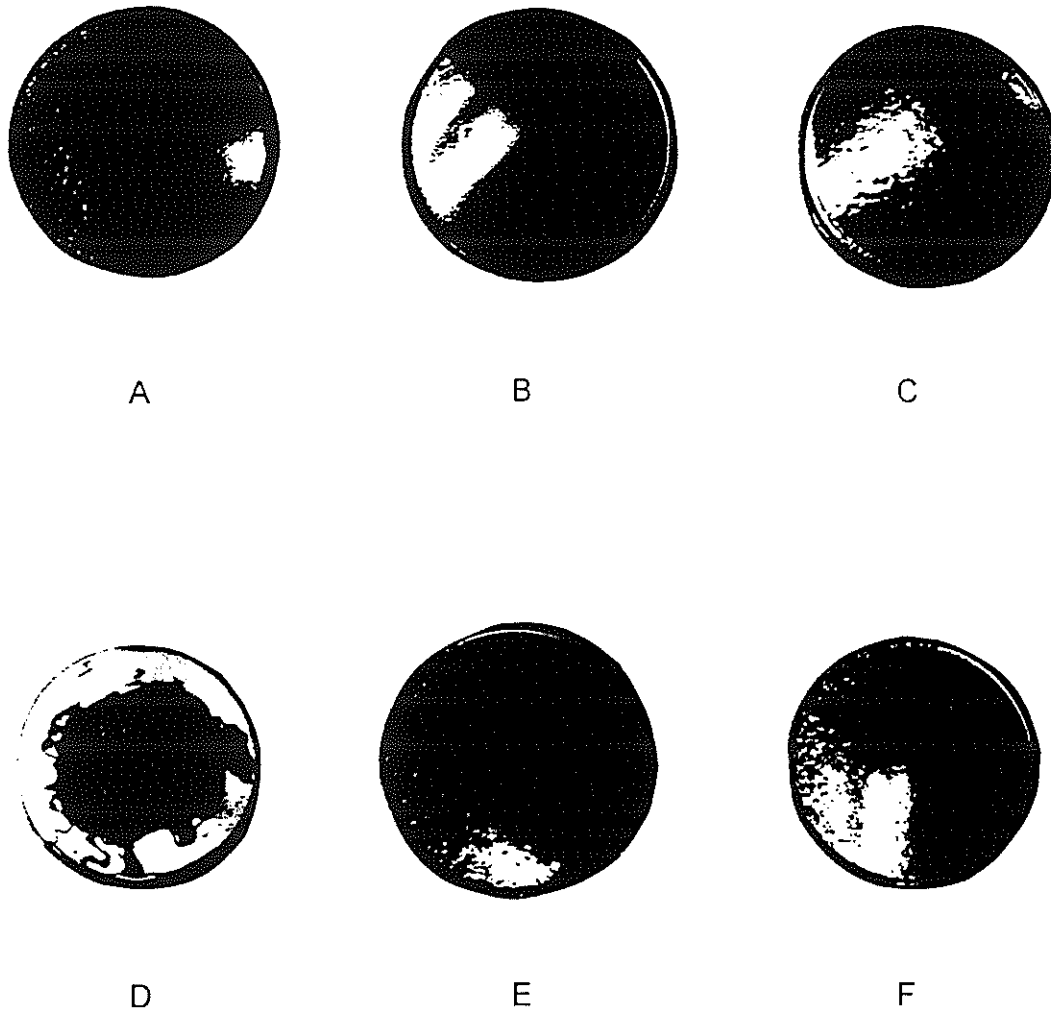


Figure 18. Separation of tire rubber particles during TFOT aging: A, Ergon AC-30 with 15%CR; B, Lion AC-10 with 15%PR; C, Lion AC-10 with 17.5%PR; D, Lion AC-10 with 22.5%PR; E, Lion AC-10 with (15%CR + 15%AO); and F, Ergon AC-30 with (15%CR + 15%AO).



## LOW TEMPERATURE CREEP RESPONSE OF ASPHALT/RUBBER BLENDS.

The dynamic shear test only provides part of the information needed to describe good asphalt properties. Further information is gained from the bending beam, BB, test. According to SHRP recommendation, when BB test data are used to verify the grade of an asphalt cement binder, the stiffness  $S(t)$  and the creep rate,  $m = d \log S(t) / d \log(t)$ , are reported at the specification temperature at  $t = 60$  sec. If  $S(t) \leq 300$  MPa, and  $m \geq 0.30$ , the sample meets the specified grade. If  $S(t) > 300$  MPa and/or  $m < 0.30$ , the sample fails the specified grade. Since the minimum grade temperature for Louisiana asphalt binders is recommended as  $-10^{\circ}\text{C}$ , the data were collected at the next lower SHRP grade temperature, i.e.,  $T = -12^{\circ}\text{C}$ . Representative results are presented in Figures 19 and 20 and all the sample data is summarized in Table 11.

An inspection of Table 11 indicates that Lion AC-10 and Marathon AC-30 and all blends with rubber and AO met the  $S(t)$  and  $m$  criteria for the chosen temperature ( $-12^{\circ}\text{C}$ ). Rather large  $m$  values accompanied by low  $S(t)$ 's were recorded for some CRAC samples, suggesting that these blend might meet the criteria for much lower temperatures. Pretreating the rubber particles with aromatic oils enhances the ductility of the mix as can be noted from the higher deformations achieved during the test. The low temperature stiffness is also lowered by the oil treatment so low temperature cracking of these mixtures should not be a problem. Thus, pretreatment of rubber with aromatic oils improves the low temperature properties of asphalt binder without significant degradation of the high temperature properties.

TABLE 11

LOW TEMPERATURE (-12°C) BBR CREEP DATA FOR AGED ASPHALT BLENDS WITH  
CRUMB RUBBER (CR), POWDER RUBBER (PR) AND AROMATIC OIL

Asphalt Binder	Load P, g	Deformation $\delta$ , mm	Measured $S_{(60s)}$ , Mpa	Estimated $S_{(60s)}$ , MPa	m value
Lion AC-10	100.3	1.494	107.87	107.74	0.3975
Lion + 15%CR	99.5	1.466	109.05	108.91	0.3676
Lion + 15%PR	100.5	3.856	42.60	42.49	0.3269
Lion + 17.5%PR	100.3	1.812	90.47	89.40	0.4955
Lion +(15%CR + 15AO)	100.7	5.359	30.71	25.24	0.5008
Eagle AC-10	100.0	-	383	-	0.2880
Eagle + 15%CR	101.1	3.982	40.75	40.68	0.3549
Ergon AC-30	100.0	-	306.40	-	0.3100
Ergon+(15%CR+15%AO)	100.1	5.254	30.61	29.6	0.4031
Marathon AC-30	100.0	-	174.80	-	0.3448

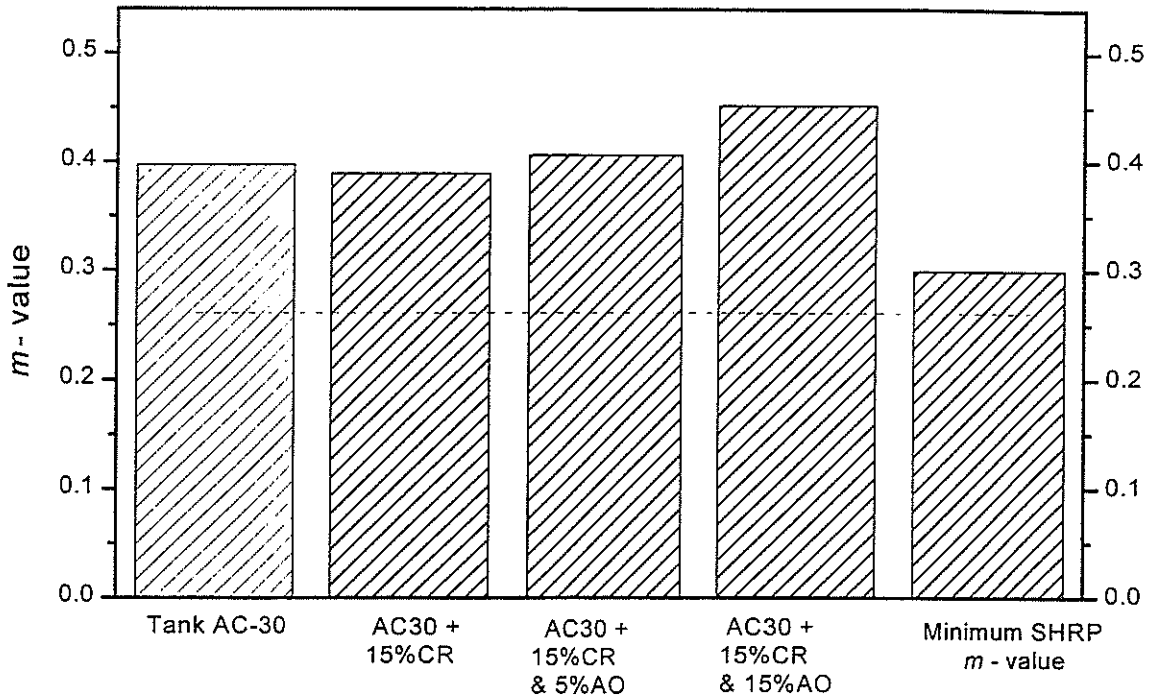


Figure 19. Bending beam low temperature creep response for tank Ergon AC-30 and blends with crumb rubber and SUN H 600T aromatic oil: the  $m$  - value.

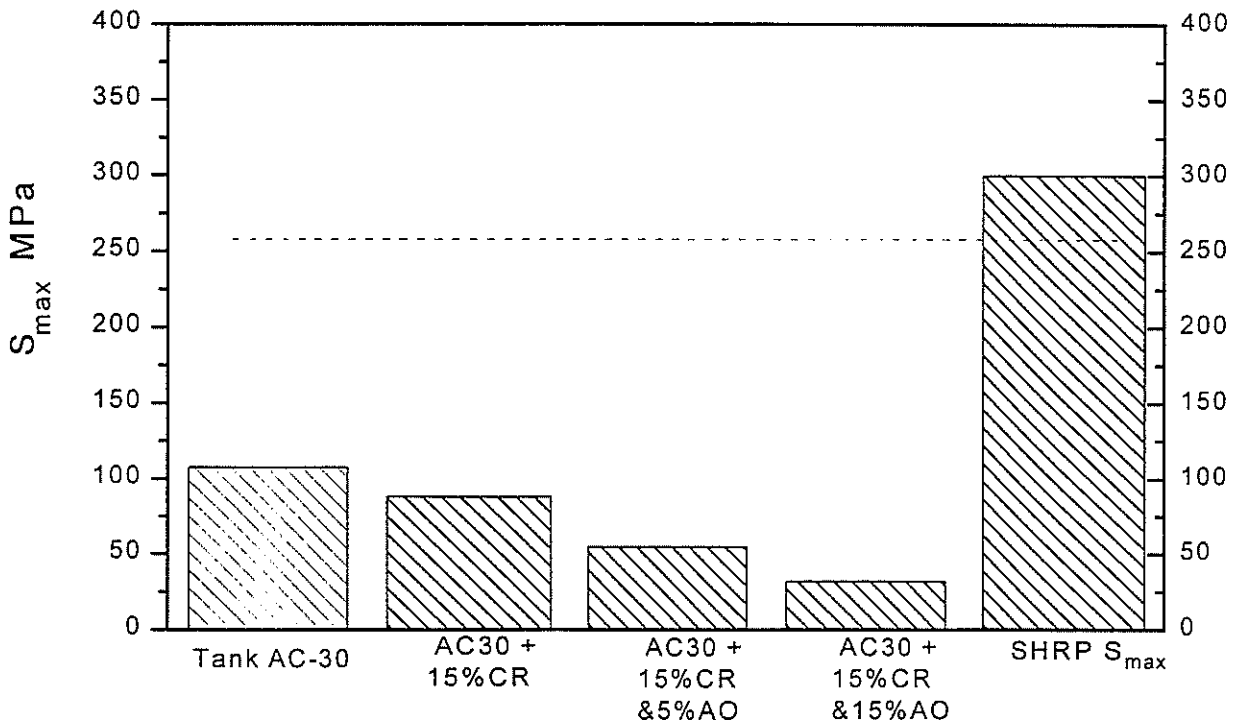


Figure 20. Bending beam low temperature creep response for tank Ergon AC-30 and blends with crumb rubber and SUN H 600T aromatic oil: the  $S_{max}$  - value

## CONCLUSIONS

The chemical composition of the asphalt is a very important parameter in determining the physical properties of RAC's. Asphalts with high aliphatic contents can induce excessive swelling of the rubber particles with a corresponding order of magnitude increase in the rheological properties. Pretreatment of the rubber particles with as little as 5 wt % aromatic oils enhances the apparent compatibility of rubber with asphalt at moderate temperatures. The protocol for addition of aromatic oils to the blend is critical, co-blending a mixture of asphalt, rubber particles and aromatic oil does not produce a blend with properties comparable to blends formed by preblending the oil with the rubber and then adding the treated particles to asphalt.

Addition of ground rubber particles to asphalt affects the performance related properties of the rubber-asphalt cement as follows:

1. The high temperature viscosity increases significantly when the rubber content exceeds 10%. The ability to prepare RAC's with 15% rubber that exhibit  $\eta @ 135^{\circ}\text{C}$  less than 3.0 Pa·s depends upon the chemical composition of the asphalt and the rubber particle size. Addition of aromatic oil moderates the high temperature viscosity; acceptable mixes containing 15% crumb rubber can be produced from AC30 grade asphalt.
2. The stiffness of the blend as reflected by  $G^*/\sin \delta$  can be enhanced several fold depending upon the concentration of rubber added. Addition of aromatic oil by preblending leads to a slight reduction in the stiffness, however, the mix still exhibits excellent high temperature properties.
3. In at least one blend, variation in the phase angle followed by  $\sin \delta$  reveal abnormal behavior of crumb rubber blends at temperatures above 60°C. Utilization of the SHRP stiffness parameter to characterize blends should be validated by assuring that  $\sin \delta$  approaches 1.0 as temperature increases to the softening point.
4. PAV aging of asphalt/crumb rubber blends reveals that these blends will exhibit long term incompatibility. The viscoelastic properties of blends containing aromatic oils follow the same trends as tank asphalts; no evidence for phase separation was detected.

However, gross phase separation of a portion of the particles was observed in the TFOT samples. Addition of the aromatic oils does not assure high temperature compatibility.

5. The low temperature creep response measured by a bending beam technique showed that pretreatment of the rubber with aromatic oil enhanced the ductility of the mix. The low temperature stiffness is also lowered by the oil treatment so low temperature cracking of these mixtures should not be a problem

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