Effect of Solvent Properties on the Viscosity of Concentrated Natural Rubber Solutions

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THE PRINCIPAL ingredients of rubber adhesives or rubber cements are rubber hydrocarbons of some type and a petroleum hydrocarbon solvent. Basically then, rubber cement is a high polymer solution of rubber in a hydrocarbon solvent. Conventional rubber solvents are straight-run C_6-C_7 distillates cut from low aromatic crudes. With the growing complexities of modern petroleum refining, the refiner now has available a substantial number of materials which could be used as rubber solvents. However, guiding principles for the selection of the proper hydrocarbons are few; boiling range is still the main criterion.

The literature teaches very little about the solution of natural rubber in a wide variety of hydrocarbon solvents at concentrations of up to 10 weight %. Much early work (*17, 25*) was done with rubber solutes at high dilution in the development of the theory of high polymer solutions. However, concerning the relationship between solvent composition and the viscosity of rubber solutions, Busse, in an exhaustive review of the literature (*8*), dismisses all the work up to 1936 as unreliable and at best qualitative, because of the extreme difficulties in studying rubber solutes which are sensitive to light, heat, acid, and oxygen. While in recent years many investigators have studied rubber solutions (*12, 14, 21*), little or no attention has been given to the factors which influence the viscosity of concentrated rubber solutions, particularly from the standpoint of solvent composition. The purpose of this study was to delineate these factors in order to furnish the petroleum refiner with a basis for selecting materials for the manufacture of rubber solvents.

CRITERIA FOR SOLVENT SELECTION

The suitability of a solvent for natural rubber cements and adhesives is judged by its volatility (which is fixed by boiling range) and by its ability to provide the desired solution viscosity at a given rubber solids content. This ability is dependent upon both the viscosity of the solvent and its solvent power, by which is meant its efficiency in dissolving and dispersing the solute (*8*). In the petroleum industry, solvent power is usually assessed in terms of the kauri-butanol (KB) value (*4*) or the aniline or mixed aniline cloud points (ACP or MACP) (*3*). These empirical tests, while useful as practical guides, are frequently misleading. As a result, there is much interest in a more fundamental measure of solvent power. Several investigators (*7, 18, 24*) have employed the solubility parameter as a measure of solvent suitability for industrially important polymers. The solubility parameter (*13*) of a substance is defined as the square root of the ratio of its energy of vaporization in calories per mole to its molar volume in milliliters at a given temperature. In systems where this parameter is applicable, an energetically favorable solvent is one whose solubility parameter most closely matches the solubility parameter of the solute.

Investigators (*5, 11, 23*) have determined by swelling measurements that the solubility parameter of slightly vulcanized natural rubber is in the range of 7.9 to 8.4. If these studies are pertinent to the viscometric behavior of concentrated rubber solutions, then the solubility parameter of an energetically favorable solvent should lie within this range.

The viscosity of concentrated natural rubber solution is dependent upon the extent to which the polymer is aggregated and the degree to which these aggregates immobilize the solvent and restrict its flow (*18*). Natural rubber hydrocarbon is a long, flexible, chain molecule made up of 1000 to 4000 monomeric isoprene units, each of which contains a highly reactive double bond (*16*). As a result, even in diluted solutions, these molecules are incorporated into relatively large molecular aggregates because of molecular entanglements, cohesive forces along the chain, and secondary valence cross linking arising from interaction of minute amounts of polar oxygenated groups equivalent to about 0.01 weight % oxygen per chain. At high concentrations, aggregation becomes much more pronounced and takes place much more readily in a poor solvent than in a good solvent. As a result, at the same concentration, a good solvent would be expected to give a less viscous concentrated rubber solution than a poor solvent (*2, 20*). This is in contrast to very diluted polymer solutions (*1*), where in an energetically favorable solvent the polymer molecule is in an uncoiled or extended state which results in a high intrinsic viscosity, whereas in an energetically unfavorable solvent the intrinsic viscosity is low because of the curling up and coiling of the polymer chains. For the rubber employed in this investigation, solutions of 4 weight % or above were regarded as concentrated solutions because the relative viscosity of such solutions were of the order of 10^3, which is considerably above the value of 1 to 2 used as criterion for dilute viscosity measurements.

Because the viscosity of a rubber solution is determined by both the viscosity of the solvent and the extent to which polymer aggregation occurs, whether or not a solvent is a good solvent energetically must be examined by a viscosity function which excludes the contribution of the solvent to the solution viscosity. Both relative viscosity and reduced viscosity fulfill this condition for concentrated solution. These are defined below:

$$\text{Relative viscosity, } \eta_r = \frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}}$$

$$\text{Specific viscosity, } \eta_{sp} = \eta_r - 1$$

$$\text{Reduced viscosity, } \frac{\eta_{sp}}{C} = \frac{\eta_r - 1}{C}$$

C is concentration in the appropriate unit. For large values of relative viscosity, characteristic of concentrated natural rubber solution, relative viscosity and specific viscosity are essentially equivalent.

The viscosity functions can be interpreted as measures of the degree of aggregation of the rubber in soltuion or of the relative attraction between solute-solute molecules and solute-solvent molecules. The more nearly alike the solute and solvent are energetically, the less is the likelihood of aggregation and the more the likelihood of solvation. Therefore, the solvent which gives the lowest relative or reduced viscosity should be the one that most closely matches the solute thermodynamically. The applicability of the solubility parameter can be judged in these terms.

EXPERIMENTAL METHODS

The rubber was a sample of commercially milled smoked sheet rubber which had been stored for several months in the dark at room temperature in contact with air. While freshly milled rubber is sensitive to heat, light, and oxygen, after a storage of 2 weeks an equilibrium is reached and the rubber remains relatively unchanged after this period.

The solvents included pure hydrocarbons, blends of pure hydrocarbons, commercial rubber solvents, and petroleum distillates in the rubber solvent boiling range. The pure hydrocarbons were of 99 mole % minimum purity and were used without further purification. The commercial rubber solvents and petroleum distillates were typical of refinery production. Pertinent properties of these solvents are listed in Table I.

Rubber solvent blends were made up at 77° F. over the concentration range of 4 to 10 grams of rubber per 100 ml. of solvent. Commercial rubber cements contain as much as 15 weight % nonvolatiles, but substantial portions of the solids are additives, such as zinc oxide and kaolin, to control bond strength, and tackiness additives, such as ester gum and other naturally occurring resins. However, to keep the systems under investigation as simple as possible, a two-component blend of the rubber solute and the hydrocarbon solvent was used in the belief that the rheological properties of this system would be a good approximation to the more complex case.

Approximately 150 grams of each blend were made up in an 8-ounce wide-mouthed jar, approximately 2-1/2 inches in diameter. Solution was effected on a small laboratory roller capable of mixing eight samples simultaneously. Rolling times of 48 and 72 hours were adopted for low- and high-concentration solutions, the 6-gram level being considered a high concentration. The viscosities of the blends did not change significantly with longer rolling times. Because of the varying composition of a bale of natural rubber and the effect of extraneous reagents on solutions of rubber, a sufficient number of rubber-solvent blends was made up (limited by the capacity of the roller) to study the effect of the desired variable completely within a single group of blends. Comparisons were then made within the group, but never from group to group unless a common link was established. These values for the effect of a particular variable on the viscosity of a rubber-solvent blend must be considered essentially relative values.

The Brookfield Synchro-Lectric viscometer, Multi-Speed Model LVF, was employed as the measuring instrument in these studies because of its widespread availability and use in rubber industry laboratories as a routine control method. It is reputed to be accurate and reproducible to ±1% of the full-scale value. Unfortunately, in measurements at low concentrations, this degree of accuracy and reproducibility had to be sacrificed to conserve sample. Nevertheless, the conclusions of this study are of general interest, because every rubber laboratory has the means to verify them.

Viscosities were measured as a function of the several variables on the Brookfield viscometer at 77° F., which was calibrated with oils of known viscosity for use without the customary guard ring, necessitated by the small containers used for the blends. Some estimate of the repeatability of the complete test procedure, from the preparation of the solution to the actual viscosity measurements, is shown in Table II for the viscosity of blends of rubber in several solvents at a concentration of 6 grams per 100 ml. of solvent and at a nominal shear rate of 6 r.p.m. All blends tabulated below a particular trial number were made up and put into solution at the same time.

RESULTS

Effect of Hydrocarbon Type. Commercial rubber solvents are constituted largely of C_6 and C_7 hydrocarbons, so blends of milled smoked sheet rubber were made up at 77° F. in each of four C_6 and C_7 pure hydrocarbons in 2-gram increments in the concentration range 4 to 10 grams per

Table I. Properties of Solvents[a]

Pure Hydrocarbons	B.P., ° F.	Molar Vol. at 77° F. Ml.	Visc. at 77° F., Cps.	MACP, ° F.	KB	Solubility Parameter at 77° F.	Analysis for Hydrocarbon Type Composition[c], Vol. %		
							A	N	P
n-Hexane	155.8	132	0.292	156	28.0	7.30			
n-Heptane	209.1	147	0.394	159	27.0	7.45			
2,3-Dimethylbutane	136.4	131	0.326	158	29.0	6.99			
2,3-Dimethylpentane	193.6	145	0.392	154	32.0	7.24			
Cyclohexane	177.3	109	0.898	119	58.5	8.20			
Methylcyclohexane	213.6	128	0.685	131	50.9	7.85			
Benzene	176.2	89	0.603	51	113.0	9.15			
Toluene	231.1	107	0.552	54	106.0	8.90			
Commercial Solvents									
Shell Tolu-Sol	202–219	134	0.502	131	41.6	7.7	9.3	56.3	34.3
Shell Sol B	144–196	134	0.325	145	31.8	7.1	7.2	9.5	82.6
Toluene raffinate	194–229	133	0.394	151	33.2	7.1	4.3	11.8	82.3
Shell rubber solvent A	170–222	132	0.457	138	41.4	7.6	2.9	57.8	39.2
Commercial hexanes	144–162	132	0.334	144	31.8	7.1	2.6	30.1	67.2
Shell rubber solvent B	114–266	130	0.359	145	33.0	7.3	2.2	30.2	67.5

[a] Values of fundamental properties of pure hydrocarbons obtained from API Research Project 44 (*2*).

[b] ASTM distillation range given for commercial distillates.

[c] Fluorescent indicator absorption analysis over silica gel. Naphthene-paraffin split by mass spectrometric analysis.

Table II. Viscosity of Various Rubber-Solvent Blends at a Concentration of 6 Grams per 100 Ml. of Solvent at a Nominal Shear Rate of 6 R.P.M.

	Viscosity at 77° F., Cps.							
	1	2	3	4	Mean	Std. Dev. of 1, Obsd.	Prob. Error of 1, Obsd.	% Error on Basis of Mean
n-Hexane	13,200	10,800	...	9,200	11,100	2015	1350	12.0
Cyclohexane	33,800	34,200	29,600	32,400	32,500	2080	1400	4.3
Benzene	10,600	7,500	8,700	...	8,900	1565	1055	11.9

100 ml. of solvent. The solvents selected were representatives of each of four hydrocarbon types: normal paraffins, *n*-hexane and *n*-heptane; branched paraffins, 2,3-dimethylbutane and 2,3-dimethylpentane; naphthenes, cyclohexane and methylcyclohexane; and aromatic, benzene and toluene. The viscosity of each blend was obtained at 77° F. at a nominal shear rate of 6 r.p.m. The data are plotted on a log-log scale in Figure 1.

The aromatic hydrocarbons yield the lowest solution viscosity, followed closely by normal paraffins and branched paraffins, with naphthenes giving the highest viscosities. These observations are similar to those of Evans and Young (*10*), who studied blends of polybutene in various pure hydrocarbon solvents in the range 0 to 10 grams per 100 ml. of solution.

Solution viscosity is plotted as a function of solvent viscosity in Figure 2 on a log-log scale and a general correlation is revealed for the nonaromatic hydrocarbons. In every case the solution viscosity of blends with aromatic hydrocarbons lies well below the base line for the paraffins and naphthenes. These results indicate that the solvent power of the aromatics as determined viscometrically must be sufficiently greater than that of the nonaromatics to compensate for relatively large solvent viscosity differences. In other words, both solvent viscosity and solvent power are important.

Blends of rubber and pure hydrocarbon solvents; shear rate, 6 r.p.m.

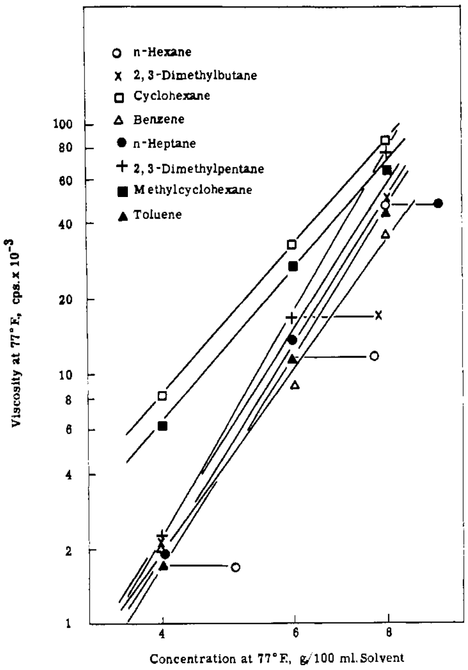

Figure 1. Viscosity of blends as a function of concentration

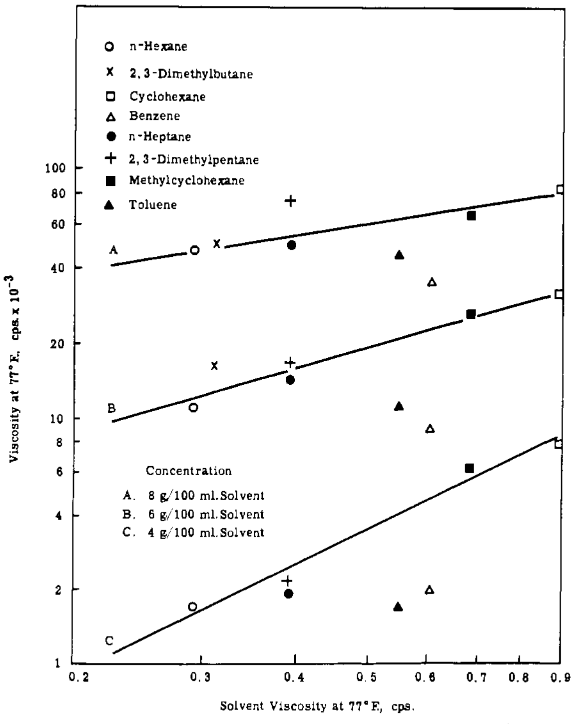

Figure 2. Viscosity of blends as a function of solvent viscosity

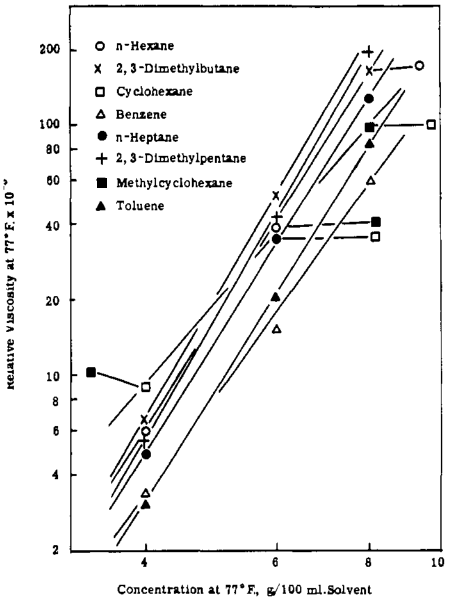

Figure 3. Relative viscosity of blends as a function of concentration

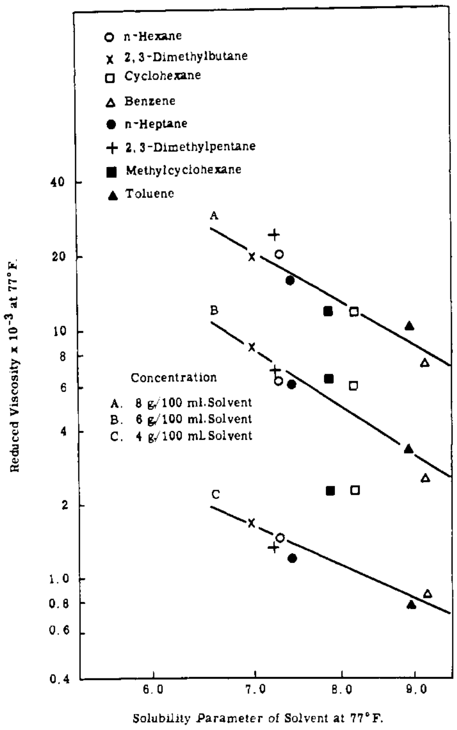

Figure 4. Reduced viscosity of blends as a function of solubility parameter

EFFECT OF SOLVENT POWER ON SOLUTION VISCOSITY

The relative viscosity of the rubber blends with pure hydrocarbons is plotted as a function of concentration in Figure 3 on a log-log scale. Aromatics give the lowest relative viscosities throughout the concentration range studied, while the relative status of the naphthenes and the normal and isoparaffins is more complex. At a concentration of 4 grams per 100 ml. of solvent, the naphthenes exhibit a higher relative viscosity than the paraffins, whereas at higher concentration the situation is reversed. The intrinsic viscosity data of Bristow and Watson (*5*) on natural rubber hydrocarbons indicate that in diluted solution the energetic favorability of the various hydrocarbon types in the C_6 and C_7 hydrocarbon family increases in the sequence: paraffins, aromatics, and naphthenes. According to Schmidt and Marlies (*20*), the plots of reduced viscosity *vs.* concentration for a good and poor solvent should cross at a concentration outside the diluted solution range. In this investigation this crossover point occurs for the naphthene and paraffin solutions in the concentration range 4 to 6 grams per 100 ml. of solvent and for aromatic and paraffin solutions at a concentration less than 4 grams per 100 ml. of solvent. These results are consistent with those of Bristow and Watson. However, comparing the naphthene and aromatic solutions no crossover is obtained. The reduced viscosity at several concentrations as a function of solubility parameter (Figure 4) indicates that the solubility parameter for natural rubber by this criterion is 9.0 or somewhat greater, which does not agree with either the results of swelling measurements or the dilute viscosity data of Bristow and Watson. This is probably because primary valence cross linking essentially nullifies the effect of secondary valence forces in swelling measurements. In the solution of unvulcanized rubber, there are no primary valence cross links. Aggregation and three-dimensional cross-linked structures, which immobilize solvent, occur as the result of secondary valence forces between the polar groups of the rubber solute. Apparently the aromatic solvents are able to disrupt these cross links and reduce aggregate size more effectively than either paraffins or naphthenes, a factor which is not evaluated in either intrinsic viscosity or swelling measurements.

Blends of Pure Hydrocarbons. To study the effect of progressive variation in solvent power and to separate the effects of solvent power and solvent viscosity, binary blends of the various possible combinations of the three C_6 hydrocarbons, *n*-hexane, cyclohexane, and benzene were made up on a volumetric basis in 10 or 20 volume % increments in the composition range 0 to 100 volume %. Viscosities of rubber-solvent blends at a concentration of 6 grams per 100 ml. of solvent were determined at 77° F. at a nominal shear rate of 6 r.p.m.

The viscosity behavior of natural rubber as a function of volumetric solvent composition for blends of benzene and *n*-hexane and of benzene and cyclohexane is shown in Figure 5. In the first instance, the resultant curve is essentially a straight line parallel to the solvent composition axis, suggesting that the increased solvent power of the solvent blend is just offset by the increased solvent blend viscosity as the benzene content of the solvent blend is increased. In the benzene-cyclohexane blends, the solution viscosity increases at a steady rate as the cyclohexane content increases, which is compatible with the higher viscosity of cyclohexane relative to benzene and the lower solvent power of cyclohexane relative to benzene.

The curves relating relative viscosity to solvent composition for blends of benzene and *n*-hexane and of benzene and cyclohexane are shown in Figures 6 and 7, respectively. The relative viscosity decreases consistently with the increase in benzene content of the solvent, reflecting the effect of the solvent power of the aromatic solvent. A correlation of relative viscosity with solubility parameter for the various blends is also shown; the solubility parameters of the blends were calculated as suggested by Hildebrand (*13*). At best this correlation can be considered only an approximation. Heat of mixing data (*6*, *15*) for binary blends of benzene, *n*-hexane, and cyclohexane over the entire concentration range give wide deviations from the values calculated from the solubility parameters of the blend components, especially for the benzene–*n*-hexane and the benzene-cyclohexane blends. It is not valid to assume that a blend of two solvents should be equivalent to a single solvent with the same solubility parameter (*22*).

As shown in Figures 8 and 9, the viscosity behavior of natural rubber in blends of *n*-hexane and cyclohexane is different from that of the benzene blends. A minimum relative viscosity is found for the blend of *n*-hexane and cyclohexane (30 volume % *n*-hexane, 70 volume % cyclohexane) whose solubility parameter is 7.9, a result which agrees with swelling measurements. An explanation for this behavior would require further study; heat of mixing measurements on this solvent pair (*15*) show only small deviation from regular solution theory in contrast with the other mixtures.

Hydrocarbon-Alcohol Blends. A small amount of alcohol added to a rubber cement reduces its viscosity and in some cases even changes a gelled cement to a thin liquid. This effect (*8*, *16*) is frequently employed in the industry to obtain the proper viscosity at a given solids content for easy application. To establish the magnitude of this effect as a function of hydrocarbon types, a brief study was made of the addition of alcohol to solutions of natural rubber in C_6 hydrocarbons.

Viscosity determinations were made at 77° F. at the concentration levels of 6 and 8 grams per 100 ml. of solvent on rubber-solvent blends in which the solvents were C_6 hydrocarbons containing 4 volume % ethyl alcohol. The results are given in Table III.

Small amounts of ethyl alcohol added to the various rubber-solvent blends reduces aggregation and hence the solution viscosity. It has been hypothesized (*8*, *16*, *20*) that the mechanism for this process is the solvation of polar groups in the rubber hydrocarbon molecule by molecules of the polar solvent, and it has been pointed out that the magnitude of the effect for a given rubber-hydrocarbon blend increases with the polarity of the alcohol. For a given alcohol added to blends of rubber in a series of hydrocarbons, the greatest viscosity reduction occurs with the poorest solvent, *n*-hexane, followed by cyclohexane, with the least reduction occurring in benzene. In *n*-hexane, the rubber molecules are in a highly aggregated state, cyclohexane is intermediate, and in benzene aggregation is at a minimum. These differences in aggregation are due to variations in the degree of solvation of the polar groups on the rubber molecule, *n*-hexane solvating these groups the least and benzene the most. Therefore, introducing solvating groups in the form of a polar solvent has a more pronounced effect on the viscosity of solutions of the poorer solvents, *n*-hexane and cyclohexane, as shown in Table III. At comparable degrees of solvation after adding ethyl alcohol, the resultant solution viscosity is a function of solvent viscosity and hence is lowest for *n*-hexane, followed by benzene, and then cyclohexane.

Commercial Rubber Solvents. Blends of milled smoked sheet rubber were made up at 77° F. in each of six commercial rubber solvents and petroleum distillates in the concentration range 4 to 10 grams per 100 ml. of solvent in increments of 2 grams. Viscosity determinations were made on each blend at 77° F. at a nominal shear rate of 6 r.p.m. The data are plotted on a log-log scale in Figure 10.

Figure 10 shows that at all concentrations, rubber solvent A is one of the poorest solvents tested as judged by the

Blends of rubber and binary mixtures of pure hydrocarbon solvents; concentration, 6 grams per 100 ml. of solvent; shear rate, 6 r.p.m.

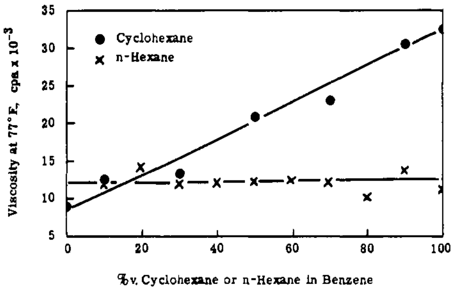

Figure 5. Viscosity of blends as a function of solvent composition

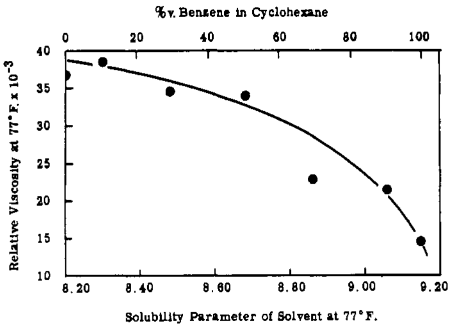

Figure 7. Relative viscosity of blends as a function of solvent composition and of solvent solubility parameter

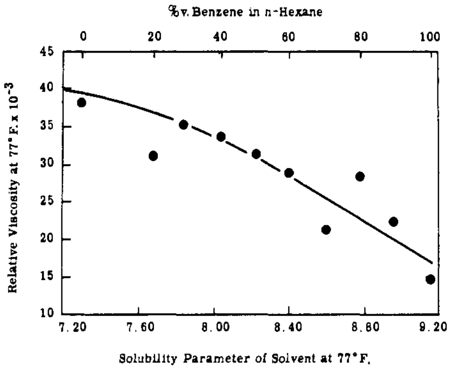

Figure 6. Relative viscosity of blends as a function of solvent composition and of solvent solubility parameter

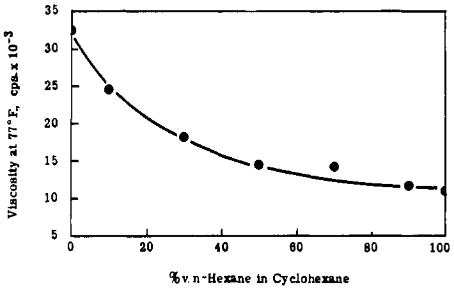

Figure 8. Viscosity of blends as a function of solvent composition

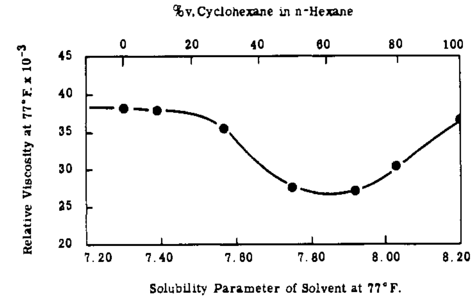

Figure 9. Relative viscosity of blends as a function of solvent composition and of solubility parameter

viscosities of its blends. This is compatible with its high solvent viscosity, high naphthene content, and low aromatic content. The relatively low mixed aniline cloud point and the relatively high kauri-butanol value indicate an appreciation of the high naphthene content by aniline and by kauri gum, not shared by the solute, rubber. The relatively high solubility parameter of rubber solvent A, 7.6, would suggest that it should be a somewhat better solvent than it is. The blend viscosities of Shell Sol B, except at the 4 grams per 100 ml. of solvent concentration, are lower than all of the other solvent blends at corresponding concentrations. This reflects the effect of the relatively high aromatic content (7.2 volume %), coupled with low naphthene content (9.5 volume %), and low solvent viscosity (0.325 centipoise). Tolu-Sol has a somewhat higher aromatic content (9.3 volume %) than Shell Sol B, a much greater naphthene content (56.3 volume %), and a much higher solvent viscosity (0.502 centipoise), which explains the uniformly high viscosities of Tolu-Sol blends at all concentrations. The relatively small differences in the blend viscosities of the rubber solvent B and commercial hexanes blends are consistent with their similar hydrocarbon composition and the small difference in solvent viscosity, 0.359 centipoise as compared to 0.334 centipoise, respectively. The viscosities of the toluene raffinate blends are comparable with those of the last two solvents at all concentrations, presumably because the somewhat higher solvent viscosity of toluene raffinate is compensated by its higher aromatic content (4.3 volume %) and lower naphthene content (11.8 volume %) compared to the other two solvents (approximately 2.5 volume % aromatic and 30 volume % naphthene). The high solvent viscosity is a consequence of its higher boiling range, indicative of higher-

Table III. Effect of Anhydrous Ethyl Alcohol on Several Viscosity Functions of Rubber-C_6 Hydrocarbon Blends at Nominal Shear Rate of 6 R.P.M.

	Viscosity at 77° F., Cps. × 10^{-3}					
	6 G./100 Ml. Solvent			8 G./100 Ml. Solvent		
Solvent	Specific	Relative	Reduced	Specific	Relative	Reduced
n-Hexane	11.1	38.0	6.16	47.0	160	20
n-Hexane + 4 vol. % anhydrous ethyl alcohol	0.80	2.66	0.28	3.20	9.6	1.2
Cyclohexane	32.5	36.2	5.86	85.5	94.5	11.8
Cyclohexane + 4 vol. % anhydrous ethyl alcohol	4.80	5.66	0.78	13.2	14.6	1.8
Benzene	8.90	14.8	2.30	35.5	58.0	7.28
Benzene + 4 vol. % anhydrous ethyl alcohol	3.00	4.08	0.68	7.50	11.7	1.5

Blends of rubber and commercial rubber solvents; shear rate, 6 r.p.m.

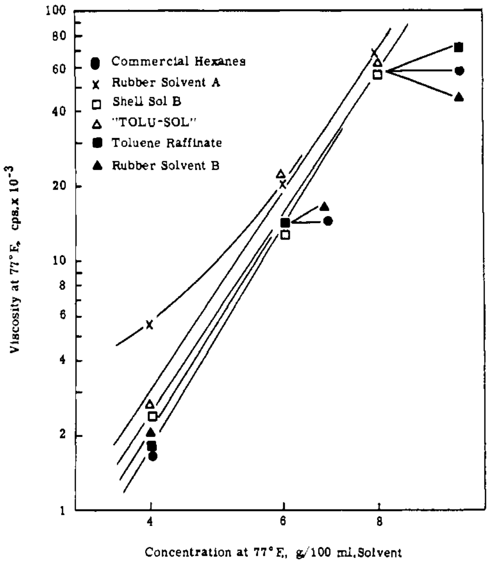

Figure 10. Viscosity of blends as a function of concentration

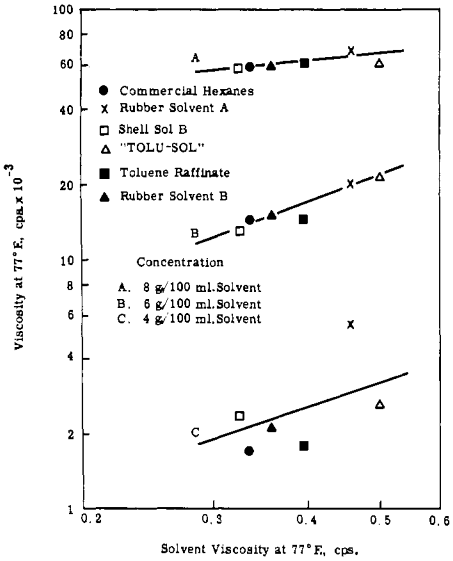

Figure 11. Viscosity of blends as a function of solvent viscosity

molecular-weight paraffins than are present in the other solvents.

The log-log plot of solvent viscosity *vs.* blend viscosity, both expressed in centipoises, in Figure 11 is again reasonably linear at all concentrations, suggesting that the solvent viscosity is the most important variable in commercial rubber solvents presumably because the spread in aromatic content (2.2 to 9.3 volume %) is not sufficient to create appreciable differences in solvent power. The large apparent differences in solvent power judged by KB and MACP shown in Table I are attributable to variations in the naphthene content.

Relative viscosities are plotted as a function of concentration in Figure 12. The relatively small spread in the data points or the tendency of the data points to cluster, particularly at the higher concentration, indicates that the state of aggregation of the rubber molecules in the various solvents is essentially the same at each concentration. This suggests that there is little variation in solvent power in commercial rubber solvents, and that the viscosity of a commercial rubber solvent is the most important variable governing its viscosity-reduction ability for rubber in commercial rubber cement formulations.

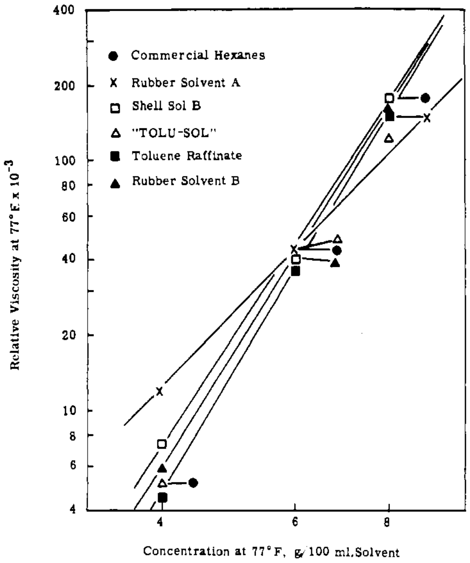

Figure 12. Relative viscosity of blends as a function of concentration

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RECEIVED for review January 12, 1959. Accepted August 3, 1959.