Solvents for Synthetic Rubbers

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The effect of solvent characteristics on the viscosity of several synthetic rubber–hydrocarbon solutions was determined. Normal and isoparaffins (C_6 and C_7) yielded lower viscosity solutions than naphthenes and aromatics at 10 weight % and 8 grams of rubber per 100 cc. of solvent, concentrations of interest to rubber cement and adhesive manufacturers. Solubility varied markedly with elastomer and solvent. Butadiene-acrylonitrile copolymer and ethylene propylene terpolymer were the least soluble; *cis*-polyisoprene, butyl rubbers, and ethylene propylene copolymer were soluble in all thinners. No general correlation was found on a solvent volume basis between solution viscosity and solvent viscosity or between relative viscosity and hydrocarbon type.

RUBBER adhesives and cements are composed essentially of natural or synthetic rubbers dissolved in concentrations of up to 15 weight % in light petroleum distillates. The solvents consist of C_6 and C_7 hydrocarbons, mainly naphthenes and paraffins with minor amounts of aromatics. Aromatic solvents are required to dissolve some synthetic rubbers.

Recently, Reynolds and Gebhart (*4*) reinvestigated the effect of solvent properties on the viscosity of natural rubber solutions. They were interested primarily in solutions in the 4 to 10 weight % range which are designated as "concentrated solutions" and differ from the dilute rubber solutions which were an integral part of the early development of polymer solution theory. The rubber used by Reynolds was a slightly vulcanized, commercially milled smoked sheet. Several pure hydrocarbons and commercial thinners were studied. Aromatics yielded the lowest solution viscosity (on a grams per 100 cc. solvent basis), followed closely by normal paraffins and isoparaffins. Naphthenes gave the highest viscosity solutions.

In the case of commercial solvents, which are mixtures of a large number of hydrocarbons of different types, Reynolds observed little variation in solvent power for natural rubber. The viscosity of a thinner was believed to be the most important variable governing its viscosity-reducing ability in rubber cement formulations.

MATERIALS

A *cis*-polyisoprene, Isoprene 500, which is similar in structure to natural rubber but contains 25 phr extender oil, was evaluated with solvents, as were the following synthetic rubbers provided by the Polymer Corp., Sarnia, Ontario: *cis*-polybutadiene, butadiene-styrene (two, of different styrene contents), butadiene-acrylonitrile, isobutylene-isoprene (butyl), and *trans*-polyisoprene. Enjay butyl HT-1068, ethylene propylene rubber (EPR), and ethylene propylene terpolymer (EPT), all obtained from Esso Research and Engineering Co., Linden, N. J., were also used in our studies. Properties and uses of these materials are given in Table I.

The behavior of the elastomers toward several pure hydrocarbons and commercial rubber solvents was determined. Pure C_6 and C_7 aliphatic, naphthenic, and aromatic hydrocarbons were used to delineate certain factors affecting solution viscosity. This was followed by measurement of viscosity of the rubber polymers in commercial thinners such as the Iosols, manufactured by Imperial Oil, Ltd., and Isopar C, a paraffinic solvent produced in experimental quantities by the Humble Oil and Refining Co. Properties of the pure hydrocarbons are listed in Table II and of the commercial solvents in Table III. The number designation of the Iosols refers to initial and final ASTM boiling points in degrees Fahrenheit—e.g., Iosol 1125 has 110° F. I.B.P. and 250° F. F.B.P.

EXPERIMENTAL PROCEDURE

Rubber solutions (some of them almost transparent) were prepared at room temperature by blending elastomer and solvent in a sealed can on a mechanical paint shaker. Comparisons were made at equal concentrations of polymer expressed as 10 weight % and/or as 8 grams per 100 cc. of thinner. The time of mixing required ranged from 3 to 16 hours, depending on the individual elastomer and the thinner. Some polymers were practically insoluble in certain solvents; others gave borderline "solutions" which did not separate but behaved erratically in the rheometer.

The viscosity of each solution was measured at 25° C. (77° F.) using a Burrell-Severs extrusion rheometer, Model A-120, manufactured by the Burrell Corp., Pittsburgh, Pa. This apparatus employs nitrogen to force the solution through a capillary tube at various shear rates. Samples of extrudate were collected at pressures of 10, 15, 20, 25, and 30 p.s.i.g., and immediately weighed. Reproducibility by this instrument of the value of Q, the quantity extruded per second, is within 5%. The experimental data were first plotted on log-log paper as extrusion viscosity *vs.* rate of shear. A linear relationship was obtained in all cases. Calculations were made using the Poiseuille equation:

$$\eta = \frac{P\pi R^4}{8LQ}$$

where

P = pressure, dynes per sq. cm.
R = radius of orifice, cm.
L = length of orifice, cm.
Q = quantity extruded, cc./sec.
η = viscosity, poises

and rate of shear = $[(4Q)/(\Pi R^3)]$ sec.$^{-1}$

PURE HYDROCARBONS

Data on the solubility and solvency characteristics of the rubber-hydrocarbon systems investigated are summarized in Table IV. Rates of shear varied between 1000 and 20,000 sec.$^{-1}$, depending on the elastomer. Hydrocarbons were compared at the same shear rate for a given solute.

The experimental data are expressed on the basis of solvency of the hydrocarbon for the rubber, using toluene as a standard. The relative solvency, or viscosity reducing power, is defined as

$$100 \times \frac{\text{viscosity of rubber in toluene, poises}}{\text{viscosity of rubber in test solvent, poises}}$$

Table I. Properties of Synthetic Rubbers

	Isoprene 500	Taktene 1202	S-630	SS-250	Krynac 803
Supplier	Shell Oil Co.		Polymer Corp., Sarnia, Ontario		
Type	...	Stereospecific	General-purpose	Self-reinforcing	Oil-resistant
Composition	*cis*-Polyisoprene[b]	98% *cis*-polybutadiene	Butadiene-styrene (28% bound styrene)	Butadiene-styrene (54% bound styrene)	Butadiene-acrylonitrile (34% bound AcN)
Unsaturation, mole %	...	...	...	...	...
Uses	...	In high impact polystyrene	Light colored goods	For low sp. gr. hard stocks	Easy processing, general purpose

Supplier	Butyl 101	Butyl HT-1068	Trans-Pip	EPR 404[a]	EPT 3509[a]
Type		Enjay Chemical Co.	Polymer Corp.	Enjay Chemical Co.	
Composition	...	...	Stereospecific	...	Terpolymer
	Isobutylene-isoprene		Very high content *trans*-polyisoprene	Ethylene (43.7%)-propylene	Ethylene (56.3%)-propylene-diene (2.7%)
Unsaturation, mole %	0.7	...	...	40 Mooney viscosity	58 Mooney viscosity
Uses	Food and drug applications	...	Synthetic balata	...	...

[a] Experimental product. [b] Contains 25 phr extender oil.

***cis*-Polyisoprene (Isoprene 500).** Since this elastomer contains 25 phr extender oil, comparisons with other rubbers should take this into account. *cis*-Polyisoprene, like natural rubber, is soluble in all the usual hydrocarbons. At equivalent weight per cent rubber, benzene and cyclohexane yielded high solution viscosities, followed by methylcyclopentane and the paraffins, *n*-hexane and 2,2-dimethylbutane (neohexane). In the C_7 series, toluene and methylcyclohexane gave equivalent viscosities and *n*-heptane, somewhat lower values.

***cis*-Polybutadiene (Taktene 1202).** Figure 1 shows the viscosity *vs.* shear rate for solutions of *cis*- polybutadiene at 10 weight % concentration in C_6 hydrocarbons. Large differences are evident between viscosities of the aromatic, naphthene, and paraffin solutions: Highest viscosities are obtained with benzene, followed by methylcyclopentane and *n*-hexane. Also shown is a plot for solutions containing 8 grams of elastomer per 100 cc. of solvent; on this basis, the differences are minimized. The same is true of C_7 hydrocarbon solutions, but in this case, the order of relative solvency is changed to : paraffin > aromatic > naphthene. This polymer is not appreciably soluble in 2,2-dimethylbutane.

Butadiene-Styrene Copolymers (Polysar S-630 and SS-250). At 10 weight % concentration of S-630, the lowest solvencies were obtained with benzene and toluene, and the highest with methylcyclopentane. Cyclohexane and methylcyclohexane were intermediate. Differences were minimized on a solvent volume basis but the same relative order prevailed.

SS-250 exhibited much larger variations. Methylcyclohexane had the highest solvency (340% of toluene). The solubility in methylcyclopentane is slightly under 10 weight % at 77° F. Paraffinic thinners dissolved only small amounts of either rubber.

Butadiene-Acrylonitrile (Krynac 803). Concentrated solutions were obtainable only with toluene and benzene. Benzene yielded higher solution viscosity than toluene (weight basis).

Isobutylene-Isoprene (Polysar Butyl 101 and Enjay Butyl HT-1068). Butyl 101 rubber dissolved readily in all hydrocarbons, giving crystal clear solutions of relatively low viscosity. On a weight per cent basis, by far the lowest viscosities were obtained with the paraffins. The highly branched 2,2-dimethylbutane yielded higher viscosity solutions than normal paraffins. The highest vescosity resulted from cyclohexane, in which respect Butyl 101 was unique.

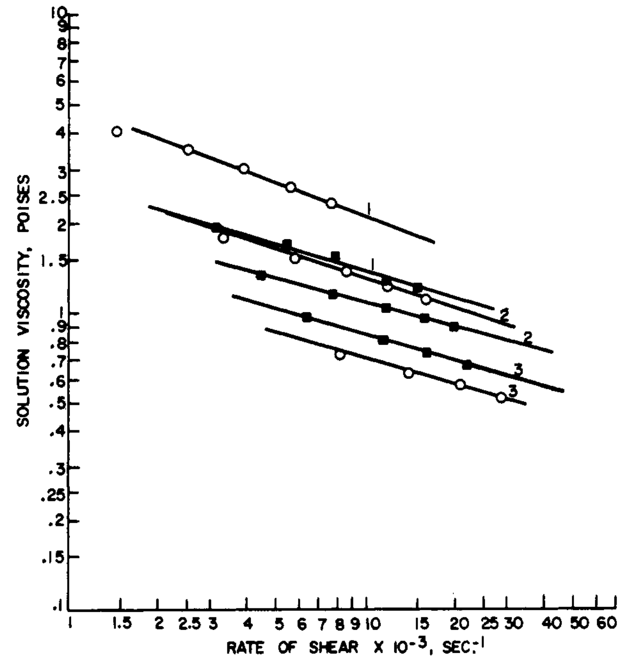

Figure 1. Viscosity of solutions of *cis*-polybutadiene in C_6 hydrocarbons as a function of rate of shear

○ 10 weight % solutions at 77° F.

■ 8 grams of rubber per 100 cc. of solvent at 77° F.

1. Benzene
2. Methylcyclopentane
3. *n*-Hexane

For the high temperature butyl, HT-1068, evaluated on a solvent volume basis, naphthenes had the lowest solvency, benzene and toluene were intermediate, and *n*-hexane, *n*-heptane, and 2,2-dimethylbutane had the greatest viscosity reducing power.

***trans*-Polyisoprene (Trans-Pip).** Only aromatic and naphthenic solvents dissolved this elastomer to an appreciable extent; toluene and cyclohexane yielded solutions of the same viscosity; benzene gave slightly higher viscosity and methylcyclopentane gave the lowest viscosity.

Table II. Properties of Hydrocarbons[a]

	C6						C7		
	Cyclopentane	Benzene[b]	Methyl-cyclopentane	Cyclohexane	*n*-Hexane	2,2-Dimethylbutane (neohexane)	Toluene[c]	Methyl-cyclohexane	*n*-Heptane
Specific gravity at 77° F.	0.745	0.875	0.742	0.773	0.658	0.649	0.863	0.767	0.680
B.P., ° F.	121	176	161	177	156	121	231	214	209
Molar volume at 77° F., cc.	94	89	113	109	132	133	107	128	147
Heat of vaporization at 77° C., cal.	6770	7900	7610	7900	7490	6780	9080	8700	8600
Solubility parameter[d]	8.1	9.1	7.9	8.2	7.2	6.8	9.0	8.0	7.4
Viscosity at 77° F., cp.	0.41	0.60	0.47	0.90	0.29	0.35	0.55	0.685	0.39
Kauri-butanol value, ASTM D 1133-61	. . .	113	47	58.5	28	26.5	106	51	27
Aniline point, ° F., ASTM D 1012-62	63	51[e]	95	119	156	Above b.p.	51[e]	131	159

[a] Phillips 99 mole % purity except where noted otherwise. [b] Imperial Oil Ltd. nitration grade. [c] Imperial Oil Ltd. pure grade. [d] Calculated from heat of vaporization and molar volume. [e] Mixed aniline pt. ASTM D 611-55T.

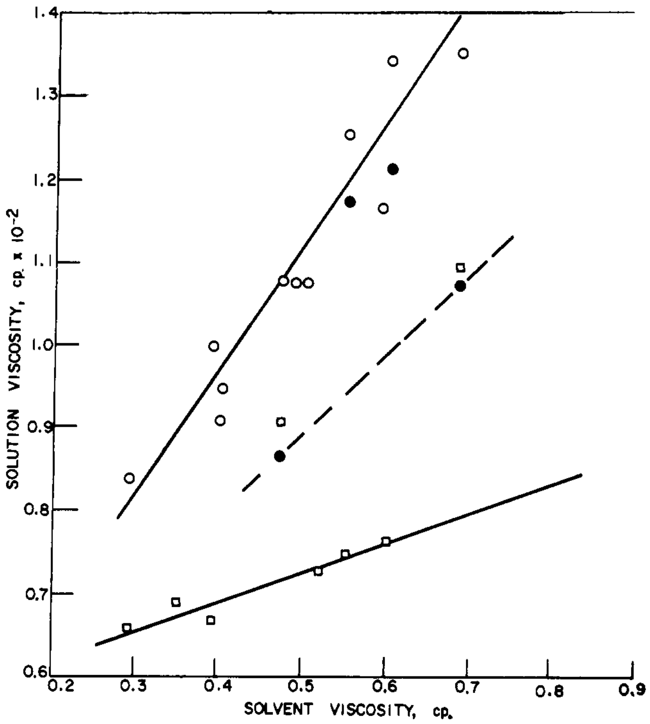

Figure 2. Viscosity of solutions of synthetic rubbers as a function of solvent viscosity

8 grams of rubber per 100 cc. of solvent at 77° F.

○ *cis*-Polybutadiene (Taktene 1202)

● Butadiene—28% styrene (S-630)

☐ Enjay butyl HT-1068

Ethylene Propylene Rubber (EPR 404). EPR 404 dissolved in all the thinners, and differences in solution viscosity were the greatest of the polymers studied. The lowest viscosities were obtained with paraffins and the highest with aromatics.

Ethylene Propylene Terpolymer (EPT 3509). With EPT 3509, the only solvent to give a concentrated solution was toluene. All others yielded only extremely fibrous, coarse suspensions.

COMMERCIAL RUBBER SOLVENTS

The data for commercial thinners are summarized in Table V. With polyisoprene, the only solvent investigated was Isopar C (chiefly mixed C_8 isoparaffins) and since it had the same solvency characteristics as toluene and methylcyclohexane, it was concluded that other commercial thinners would have about the same solvency for this elastomer.

In the case of the other synthetic rubbers, there were marked differences in solubility. Four elastomers—Krynac 803, Trans-Pip, SS-250, and EPT 3509—would not dissolve in commercial thinners. Taktene 1202 and S-630 were soluble in paraffin-naphthene-type solvents but not in isoparaffins. The butyls and EPR 404 dissolved in all solvents used. With *cis*-polybutadiene, the greatest viscosity reduction on a weight basis was obtained with thinners containing hydrocarbons of the lowest molecular weight (Iosols 1520 and 1125). These are also less aromatic than the higher boiling petroleum fractions, Iosols 2024 and 2429, and have higher paraffin-naphthene ratios. Normal paraffins had the highest solvency while the isoparaffin, neohexane, is a nonsolvent. The low solvent power of isoparaffins was confirmed by Isopar C, which dissolved only 1 weight % of polymer. On a solvent volume basis, lowest viscosities resulted from the low molecular weight thinners.

With the butadiene-styrene copolymer S-630, the lowest viscosity solutions were obtained with Iosol 2024. Based on

Table III. Properties of Commercial Rubber Solvents

Iosol 1125	Iosol 1125	Iosol 1520	Iosol 1921	Iosol 2024	Iosol 2429	Isopar C[a]
Specific gravity, at 77° F.	0.716	0.718	0.744	0.748	0.767	0.716
ASTM boiling range, ° F.	110–250	150–200	190–210	200–240	239–290	210–225
Mid B. pt., ° F.	185	161	198	208	254	215
Molar volume at 77° F., cc.	134	123	130	135	148	152
Heat of vaporization at 77° F., cal.	8100	7570	8360	8560	9570	8740
Solubility parameter	7.5	7.5	7.7	7.7	7.8	7.3
Viscosity at 77° F., cp.	0.40	0.40	0.49	0.50	0.59	0.52
Kauri-butanol value, ASTM D 1133–61	36.5	37	40	40.5	40.5	27.1
Aniline point, ° F., ASTM D 1012–62	128.5	127.5	123	122	122	164
Hydrocarbon type composition[b], vol. %						
Aromatics	4	4	3	7	11	...
Naphthenes	8	36	45	41	41	...
Paraffins	88	60	52	52	48	≅100

[a] Experimental product of Humble Oil and Refining Co. All others are commercial products of Imperial Oil, Ltd. [b] Fluorescent indicator absorption (FIA) analysis over silica gel. Naphthene-paraffin split by mass spectrometer is approximate only.

the behavior of S-630 with pure aromatics and naphthenes, Iosol 2429 was expected to yield lower viscosity solutions, but the effect appears to have been counteracted by its higher average molecular weight. The other two Iosols yielded "solutions" that were not quite homogeneous and so gave inconsistent results on the rheometer.

The butadiene copolymer of higher styrene content, SS-250, was not sufficiently soluble in commercial solvents.

Solvency differences with Butyl 101 were significant. Iosol 1125, Iosol 1520, and Isopar C gave lower viscosities than the others. With Enjay Butyl HT-1068, on a gram per 100 cc. basis, the only commercial solvent tested, Isopar C, yielded solutions of the same viscosity as toluene. Iosols 1125 and 1520 gave the lowest viscosity solutions of EPR 404 and Iosol 2429 the highest.

It appears that the lowest boiling rubber solvents are the most generally useful to the manufacturer of cements and adhesives. Although a high paraffin content is usually desirable for maximum viscosity reduction, a small residual amount of aromatics is often essential to dissolve the the rubbers sufficiently. Optimization of solvent properties by blending is a field well worth exploring for a specific elastomer. Reynolds (*4*) and others have shown that certain nonsolvents may be added in minor amounts to modify viscosity characteristics of natural rubber solutions. This may also apply to synthetic rubbers, even those that appear to be soluble only in pure aromatics—e.g., butadiene-acrylonitrile, and ethylene propylene terpolymer.

DISCUSSION OF RESULTS

Relative Solvency. The experimental data for pure hydrocarbons, summarized in Table IV, were averaged for systems capable of yielding 10 weight % solutions or 8 grams of rubber per 100 cc. of solvent. In order of decreasing solvency, relative to toluene, the hydrocarbons are as follows:

	Relative Solvency	
	10 wt. % solution	8 g./100 cc. solvent
n-Hexane	240	132
n-Heptane	205	120
2,2-Dimethylbutane (neohexane)	195	...
Methylcyclopentane	155	108
Methylcyclohexane	150	90
Cyclohexane	115	...
Toluene	100	100
Benzene	92	96

These data indicate the order of relative solvency to be: paraffins > naphthenes > aromatics on a weight basis; and paraffins > (naphthenes ≈ aromatics) on a solvent volume basis. Paraffins are limited in their utility by the low solubility of some elastomers in them, when sufficient compatibility does exist, paraffins are potent viscosity reducers.

Solvent Viscosity. Burrell (*1*) concluded that the viscosity of polymer solutions is proportional to the viscosity of the solvents and quoted data of Streeter and Boyer (*6*) on polystyrene as proof of this postulate. Burrell presented a graph showing viscosity of 12 weight % polystyrene solutions as a linear function of solvent viscosity. Reynolds and Gebhart (*5*) believed solvent viscosity to be the most important factor governing reduction of long oil alkyd resins. Our results on alkyds were not in general agreement with that theory, except for members of a homologous series of paraffinic hydrocarbons when used with resins of very high oil content (*3*).

Reynolds and Gebhart in their later study of thinners for natural rubber again emphasized the effect of solvent viscosity (*4*). For nonaromatics only a linear correlation was observed between solvency for natural rubber and viscosity of the thinner; aromatics gave solution viscosities much lower than predicted and did not fit the correlation at any solids content (4, 6, or 8 grams per 100 cc. of solvent).

In Figure 2 are shown solution viscosities of three synthetic rubbers (determined at a concentration of 8 grams of solute per 100 cc. of solvent) plotted against solvent viscosity. Data on commercial thinners are included. A reasonably linear correlation is obtained for one elastomer, *cis*-polybutadiene, but not for the other two. In the case of butadiene-styrene, the aromatic hydrocarbons, benzene and toluene, give abnormally high solution viscosities and with the butyl rubber all three naphthenes yield solutions of very high viscosity. Thus, it may be concluded that no general correlation exists between viscosity oa synthetic rubber solutions and that of the solvent at the concentration studied. The deviations are evidently due to varying degrees of molecular association of the solute in different solvents, even at the relatively high rate of shear used.

In concentrated polymer solutions, there is an equilibrium between solvation and aggregation (molecular association). Increase in the number of large molecular aggregates is generally assumed to increase the viscosity of the solution. Hence, thinners such as paraffinic hydrocarbons which are generally "poor" solvents and do not readily solvate polymer, but promote aggregation instead, yield solutions of high viscosity. Concentrated solutions (25 to 50 weight %) of alkyds in paraffins are considered to be highly aggregated. Paraffins are poorer solvents than aromatics for alkyd resins; solubility is lowered in paraffins and solution viscosity is usually much higher at the same resin concentration (*3*).

Table IV. Relative Solvency[a] of Hydrocarbons for Synthetic Rubbers at 77° F.

(Solutions of 10 wt. % rubber except as indicated)

Rate of Shear, Sec.$^{-1}$	*cis*-Poly-isoprene[b] 10,000	Taktene 1202 10,000	S-630 10,000	SS-250 5,000	Krynac 803 20,000	Butyl 101 10,000	Enjay Butyl HT-1068 10,000	Trans-Pip 5,000	EPR 404 1,000	EPT 3509 1,000
Cyclopentane	...	...	...	...	...	120	...	...	212	...
Benzene	93	93;93[c]	91;97[c]	78	83	89	97[c]	94	110	...[d]
Methylcyclopentane	123	150;117[c]	181;126[c]	<10%[d]	...	117	82[c]	155	205	...
Cyclohexane	97	108	118	195	...	65	70[c]	100	124	...
	148	280;150[c]	<2%[e]	<3%[e]	...	214	113[c]	<2%[e]	320	...
2,2-Dimethylbutane(neohexane)	148	Sl. sol.	Sl. sol	0.5%[e]	...	135	108[c]	Sl. sol.	300	...
Toluene	100	100;100[c]	100;100[c]	100	100	100	100[c]	100	100	100
Visoosity, poises	1.85	1.95;1.26[c]	1.74;1.18[c]	2.4	0.62	0.96	0.75[c]	3.0	22.5	10
Methylcyclohexane	100	130;93[c]	130;109[c]	340	...	93	68[c]	125	136	...
n-Heptane	137	250;130[c]	2.5%[e]	<5%[e]	...	172	110[c]	<2%[e]	260	...

[a] Relative solvency = $\dfrac{100 \times \text{viscosity of rubber in toluene, poises}}{\text{viscosity of rubber in test solvent, poises}}$ at rate of shear indicated for each system. [b] Contains 25 phr extender oil, so solutions contain 8 wt. % rubber. [c] At concentration of 8 g. rubber/100 cc. solvent. [d] Large agglomerates, not homogeneous. [e] Saturated solution.

Table V. Viscosity of Commercial Solvent-Rubber Solutions at 77° F.

(Solutions of 10 wt. % rubber[a], viscosity in poises)

Rate of Shear, Sec.$^{-1}$	*cis*-Poly-isoprene 10,000	Taktene 1202 10,000	S-630 10,000	SS-250 5,000	Butyl 101 10,000	Enjay Butyl HT-1068 10,000	EPR 404 1,000
			Viscosity, Poises				
Iosol 1125	...	0.98;0.95[b]	...	...	0.58	...	10.2
Iosol 1520	...	0.94;0.91[b]	...	...	0.63	...	10.3
Iosol 1921	...	1.20;1.08[b]	0.97	3.5%	0.76	...	11.3
Iosol 2024	...	1.20;1.08[b]	0.79	...	0.74	...	13.0
Iosol 2429	...	1.33;1.17[b]	0.97	...	0.78	...	14.2
Isopar C	1.83	1%	<2%	Trace	0.66	0.73	...

[a] Krynac 803 (butadiene-acrylonitrile), Trans-Pip (*trans*-polyisoprene), and EPT 3509 (ethylene propylene terpolymer) were practically insoluble in these thinners. [b] At concentration of 8 g. rubber/100 cc. solvent.

Table VI. Relative Viscosity of Solutions of Synthetic Rubbers

$\eta_{\text{rel}} = \eta$ solution/η solvent; 8 grams rubber/100 cc. solvent at 77° F.

	cis-Polybutadiene		Butadiene-28% Styrene		Enjay Butyl	
Rate of Shear, Sec.$^{-1}$	10,000	1,000	10,000	1,000	10,000	1,000
n-Hexane	290	520	Sl. sol.		230	500
Neohexane	Sl. sol.		Sl. sol.		200	400
n-Heptane	260	490	Sl. sol.		170	230
C_8 isoparaffins	Sl. sol.		Sl. sol.		140	200
Methylcyclopentane	200	425	170	330	190	450
Cyclohexane	...	...	...	...	120	235
Methylcyclohexane	200	440	160	315	160	425
Benzene	225	460	200	410	130	270
Toluene	230	480	215	440	135	250

Reynolds (*4*) states that "a good solvent would be expected to give a less viscous concentrated rubber solution than a poor solvent," because of more molecular aggregate formation in the poor solvent. Our data on synthetic rubber solutions (Figure 2) indicate an increase in solution viscosity when naphthenes or aromatics are used as thinners for synthetic rubbers. This behavior is in distinct contrast to that of most alkyds with hydrocarbons of different type.

Part of the viscosity increase in the case of synthetic rubbers is due to the higher viscosity of naphthenes and aromatics as compared to paraffins. This is not the only reason, however, since with butadiene-styrene copolymer aromatics yield abnormally high solution viscosities and naphthenes have the same effect with the butyl rubber. The observed differences are too large to be accounted for except by varying degrees of molecular association of the solute.

It is common practice in rheological work to eliminate the effect of solvent viscosity by referring to relative viscosity, η_{rel}, which is defined as $\eta_{\text{solution}}/\eta_{\text{solvent}}$. Reynolds and Gebhart found that solutions of natural rubber in aromatics had the lowest relative viscosities throughout the concentration range studied.

Relative viscosities were calculated for three of our synthetic rubber-hydrocarbon systems at a concentration of 8 grams of solute per 100 cc. of solvent and two rates of shear (10,000 and 1000 sec.$^{-1}$). The data are given in Table VI. No simple correlation is apparent between relative viscosity and hydrocarbon type for any of the elastomer-solvent combinations. Specifically, there is no indication of consistently lower relative viscosities with aromatic thinners, as Reynolds found with natural rubber solutions.

This does not rule out the probability of varying degrees of aggregation of synthetic rubbers in these solvents, since Doty, Wagner, and Singer (*2*) demonstrated that molecular association is possible without significant increase in viscosity. They concluded that there was molecular association of poly(vinyl chloride) (0.25 to 1.0%) solutions in dioxane at various temperatures because eightfold decrease was observed in weight-average molecular weight with increase in temperature from 25° to 60° C., although the specific viscosity ($\eta / \eta_0 - 1$) was practically unchanged in that temperature range. From these results they concluded that the molecules in the associated clusters are so tightly coiled and packed that the viscosity is reduced to almost the same value as the unassociated molecules at the same concentration.

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Rearrangement

The Composition of Cycloalkenes and Alcohols Produced by Demjanov Rearrangement of Cyclohexanemethylamine

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Denjanov rearrangement of cyclohexanemethylamine was reinvestigated, yielding as products 1-methylcyclohexene (10.2%), 3-methylcyclohexene (0.9%), methylenecyclohexane (7.9%), cycloheptene (5.4%), 1-methylcyclohexanol (17.9%), 2-methylcyclohexanol (1.2%), cyclohexanemethanol (14.8%), and cycloheptanol (24.3%). The composition of the product was determined by gas chromatography and NMR spectroscopy.

DURING an investigation (*4*) of rearrangements in cyclohexane series, it became necessary to know the composition of cycloalkenes produced by Demjanov rearrangement of cyclohexanemethylamine. Although a few groups of workers (*7, 8, 9*) have investigated this reaction, there is a lack of data for the cycloalkene composition in spite of its relatively high yield.

Each component in the cycloalkene mixture from cyclohexanemethylamine was separated by preparative scale gas chromatography and identified by comparison of its retention time and NMR spectrum with those of an authentic sample. Quantitative analysis of the cycloalkene mixture by NMR spectroscopy was in good agreement with that obtained by gas chromatography as shown in Table I. Examination of the alcohol fraction from the amine by gas chromatography revealed the presence of 2-methylcyclohexanol in addition to the three isomeric alcohols reported by Smith and Baer (*8*), but its configuration remained unidentified. NMR analysis failed to detect this alcohol, however. 1-Methylcyclohexanol was formed in much higher amounts than reported by Smith and Baer—17.9% instead of 2%.