may mean a pore diameter of roughly 7.5 A. which is about the distance between the graphitic planes in the crystallites (*7*).

Columns 2 and 3 of Table III show the relative weight losses of the black in case of oxidation to carbon dioxide and monoxide, respectively.

SUMMARY

Porous blacks of high surface area can be produced without changing particle size either directly, in the normal furnace black process, or indirectly, in the laboratory by the air oxidation of a normal commercial and essentially nonporous HAF black raw material. Blacks of high surface area produced by the direct process are characterized by a retardation in rate of vulcanization, lower rebound resilience, and high electrical conductivity. Laboratory-prepared products of high area show cure retardation, but their electrically conductive and resilience properties show relatively little dependence on degree of porosity and surface area. Bound rubber measurements, modulus, tensile, and abrasion properties of the laboratory-oxidized samples indicate an increase in reinforcement with increasing surface area.

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Polymers of Butadiene with Monomers Containing Nitrile, Carboxyl, and Nitro Groups

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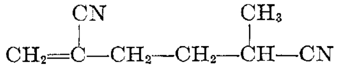
NEED for an oil-resistant rubber that possesses good low temperature properties has led to the investigation of a number of monomers which seemed to be potentially useful for this purpose in a butadiene copolymer or terpolymer.

This paper describes the results of three projects in this field. The first group of products studied are terpolymers of butadiene, acrylic acid, and acrylonitrile which were suggested by Paul Greer as interesting because butadiene copolymers with acrylic acid and with acrylonitrile both have oil resistance and the acrylic acid copolymers have good low temperature properties (*8*).

The second group of polymers studied make use of a new monomer (*7*), α-methylene-δ-methyladiponitrile (I), which seemed to offer promise because of the two nitrile groups and the alpha-side chain which might be expected to lower the freeze point of the copolymer (*11*). Both its copolymers with butadiene and its terpolymers with butadiene and acrylonitrile have been prepared.



$$CH_2{=}\underset{}{\overset{CN}{C}}{-}CH_2{-}CH_2{-}\overset{CH_3}{CH}{-}CN$$

I

The third group of polymers are copolymers of butadiene with a number of acrylic acid esters of cyanohydrins and a nitro alcohol. Butadiene copolymers of acrylic esters have shown good low temperature properties (*8*) and it was thought the nitrile and nitro substituents in these esters might confer oil resistance on a copolymer.

Butadiene–Acrylic Acid–Acrylonitrile Terpolymers. Terpolymers have been successfully prepared in a sodium alkane sulfonate emulsion with azobisisobutyronitrile as the initiator and technical mixed straight-chain mercaptans (about C_{12}) as modifier at 60° C. (*9*). The terpolymers show infrared absorption at 2232 cm.$^{-1}$ which indicates the presence of nitrile groups and at 1712 cm.$^{-1}$ which indicates carboxyl groups. The polymers are soluble in benzene and have inherent viscosities in the range of about 0.9 to 1.8. Some details of the preliminary experiments are listed in Table I.

Table I. Terpolymers from Butadiene, Acrylic Acid, and Acrylonitrile

(Azobisisobutyronitrile initiated at 60° C.)

Charge Ratio (Butadiene/Acrylic Acid/Acrylonitrile), G./Ml./Ml.	Modifier, Mg.	Time, Hr.	Conversion, %
17/2/1	75	9	49
17/1.5/1.5	50	7.8	40
17/1.5/1.5	50	8.3	40
17/1/2	50	6.8	40
17/1/2	50	8.3	60
17/1.5/1.5	50	9.3	53

Some evaluation samples were prepared from charging stocks which contained 85.8 to 88.5 parts of butadiene, 4 to 8.2 parts of acrylonitrile, and 5.1 to 10.1 parts of acrylic acid. The polymers were purified and analyzed for nitrogen to determine the amount of acrylonitrile incorporated, which ranged from 6.1 to 12.9%. The incorporated acrylic acid determinations are not considered very accurate since they are based on oxygen content determined by differences.

The stress-strain by microtechnique (*5*), low temperature flexibility (*4*), low temperature retraction (*12*), oil resistance (*3*), and hysteresis-temperature rise (*2*) properties of these terpolymers were determined by standard procedures. These terpolymers show stress-strain properties that are slightly inferior to standard GR-S; their low temperature flexibility is slightly better than GR-S and better than a butadiene (82)–acrylonitrile (18) copolymer although they show more tendency to crystallize than GR-S; their oil resistance is superior to GR-S but considerably less than that of the butadiene-acrylonitrile copolymer control; their hysteresis-temperature rise properties are poorer than those of GR-S.

α-Methylene-δ-Methyladiponitrile Copolymers and Terpolymers. Copolymers of α-methylene-δ-methyladiponitrile with butadiene and terpolymers of these two monomers and acrylonitrile have been prepared in the mutual recipe (original standard recipe, *14*) at 50° C., as shown in Table II. Nitrogen analyses indicated that these copolymers and all those made for evaluation were slightly richer in the dimer than was the charge ratio.

Table II. Copolymers of Butadiene and α-Methylene-δ-methyladiponitrile

(Mutual recipe with potassium persulfate initiation at 50° C.; 0.05 gram of modifier per 20 grams of monomers)

Charge Ratio (Butadiene/ α-Methylene-δ-methyladiponitrile)	Time, Hr.	Conversion, %	Benzene Soly., %	Inherent Viscosity
95/5	3.25	24	100	2.1[a]
	4.25	42	100	3.2
	5.25	56	98	3.1
	5.75	67	100	2.6
	6.25	75	100	2.1
85/15	3.25	36	100	1.6
	4.25	52	100	2.3
	5.25	69	100	2.3
	5.75	76	100	2.1
	6.25	82	100	1.7

[a] Nitrogen content 2.28%; comonomer incorporated 10.9%.

In Table III are recorded some data on terpolymers which indicate that both the acrylonitrile and α-methylene-δ-methyladiponitrile are incorporated in the terpolymers, although it is not possible to determine the exact amounts of either present in these products. These polymers were used as evaluation samples.

Table III. Terpolymers of Butadiene, Acrylonitrile, and α-Methylene-δ-methyladiponitrile

(Modifier 0.05 gram per 20 grams of monomers)

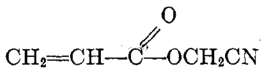
Illinois Sample No.	Charge Ratio (Butadiene/ Acrylonitrile/ α-Methylene-δ-methyladiponitrile)	Conversion, %	Nitrogen, %		
			Max. if only acrylonitrile incorporated	Max. if only dimer incorporated	Found
287	87/9/4	66	3.60	1.27	5.12
289	88/6/6	64	2.48	1.96	3.81
291	88/4/8	63	1.68	2.65	3.74

In each case the nitrogen content of the terpolymer exceeds the maximum theoretically possible if only one nitrile had entered the chain.

In addition to these evaluation samples others are described in this paper. The oil resistance of the copolymers does improve with increased nitrile content. Freeze resistance, however, simultaneously decreases. There is very little difference in the freeze point and oil resistance of samples in which an equal weight acrylonitrile replaces the α-methylene-δ-methyladiponitrile.

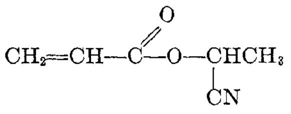
Copolymers of Butadiene and Acrylate Ester of Cyanohydrins. The patent literature (*1*) claims that copolymers of butadiene with the acrylate and with the methylacrylate of 2-methyl-2-nitropropanol and with the methylacrylate of the cyanohydrins of formaldehyde, acetone, and ethylene show solvent and oil resistance but does not give information on the low temperature properties of these copolymers. The acrylates of these cyano and nitro alcohols as well as of acetaldehyde cyanohydrin have been prepared and copolymers with butadiene have been made.

The esters (II to VI) were prepared from acrylyl chloride and the cyanohydrins derived from formaldehyde, acetaldehyde, acetone, and ethylene and from 2-methyl-2-nitropropanol, respectively. The procedure was adapted from the Organic Syntheses preparation of acetates from acetyl chloride and alcohols in the presence of dimethylaniline (*6*).



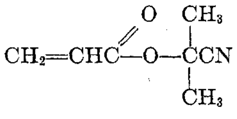
$\mathrm{CH_2{=}CH{-}\overset{O}{\overset{/\!/}{C}}{-}OCH_2CN}$

II



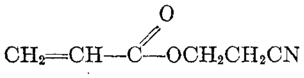
$\mathrm{CH_2{=}CH{-}\overset{O}{\overset{/\!/}{C}}{-}O{-}\underset{CN}{\underset{|}{C}}HCH_3}$

III



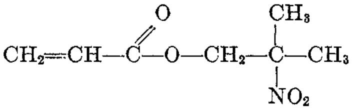
$\mathrm{CH_2{=}CH\overset{O}{\overset{/\!/}{C}}{-}O{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}CN}$

IV



$\mathrm{CH_2{=}CH{-}\overset{O}{\overset{/\!/}{C}}{-}OCH_2CH_2CN}$

V



$\mathrm{CH_2{=}CH{-}\overset{O}{\overset{/\!/}{C}}{-}O{-}CH_2{-}\overset{CH_3}{\overset{|}{\underset{NO_2}{\underset{|}{C}}}}{-}CH_3}$

VI

Purification of these esters was accomplished by employing the special techniques described in the experimental work. If precautions were not taken the monomers polymerized before distillation could be effected, even in the presence of various inhibitors such as hydroquinone, quinone, cupric acetate, cupric butyl phthalate and combinations of these.

The copolymerizations of cyanomethyl(II), 1-cyanoethyl(III), 2-cyanoethyl(V), and 2-methyl-2-nitropropyl(VI) acrylates with butadiene were achieved using the cumene hydroperoxide recipe (*13*). 2-Cyano-2-propyl acrylate(IV) was copolymerized with butadiene in the mutual recipe (*14*). Because of the tendency of the cyanoalkyl esters to homopolymerize in the soap solution before the other ingredients could be added, a special technique for accomplishing the polymerizations had to be developed.

The polymerization of 1-cyanoethyl acrylate, selected as representative of the other esters, was studied in some detail. It was observed that the rate of polymerization of systems containing small amounts of this acrylate (10 to 15%) was about twice as fast as that of butadiene for similar conversions, but as the percentage of acrylate was increased, the rate of polymerization steadily decreased. As the percentage of acrylate was increased, the solubilities in benzene and inherent viscosities of the copolymers decreased.

The percentage of acrylate incorporation of several purified 90/10 and 85/15 butadiene/1-cyanoethyl acrylate copolymers was established by elemental analyses. The results of these analyses showed that essentially all of the acrylate in the original charge was incorporated into the copolymers.

A series of experiments was carried out to study conversion versus time of tumbling. The resulting copolymers were then reprecipitated and the monomer incorporation, from 90/10 charges, was established by elemental analyses. Except for the 1-hour sample (the 0.5-hour sample was completely soluble in methanol and could not be reprecipitated) the nitrogen content varied only over a 0.7% range, corresponding to a 6% range of incorporated acrylate. These results would indicate that polymerization proceeds at a fairly even rate for both the monomers and that the ratio of butadiene to acrylate in the copolymers remains fairly constant after the first hour. Essentially all of the acrylate charged was incorporated in the 5-, 5.5-, and 6-hour co-

Table IV. Copolymers of Nitro and Cyanoalkyl Acrylates with Butadiene

Monomer Charge Ratio	Modifier, G.	Time, Hr.	Conversion, %	Soly. in Benzene, %	Inherent Viscosity in Benzene	Calcd. Acrylate in Polymer, %	N in Polymer, %
CUMENE HYDROPEROXIDE RECIPE AT 0° C.							
Butadiene/1-Cyanoethyl Acrylate							
90/10	0.114	6	62.5	95.2	2.8	17.1	1.92
90/10	0.114	6	61.5	97.2	2.4	17.1	1.91
85/15	0.114	6	58.5	80.8	2.4	27.3	3.06
85/15	0.209	6	47.5	92.8	2.5	...	...
90/10	0.114	6	55	92.4	2.8[a]	18.3	2.05
Butadiene/2-Cyanoethyl Acrylate							
95/5	0.04	10	50	100	2.6	...	...
90/10	0.04	11	49	100	2.9	8.6	0.96
90/10	0.04	14	72	86	2.5	...	...
80/20	0.04	13	61	100	2.4	...	...
85/15	0.04	15	80	99	1.8	10.1	1.13
85/15	0.04	14	68.5	100	1.93[b]	10.3	1.16
Butadiene/Cyanomethyl Acrylate							
90/10	0.114	5	43	58.4	1.3	...	...
90/10	0.152	5	43	61.2	1.3	...	...
90/10	0.152	6	48	52	1.2[c]	25.5	3.22
Butadiene/2-Nitro-2-propyl Acrylate							
95/5	0.04	11.5	56	89	4.1	...	...
95/5	0.04	12.5	63	98	4.1	...	...
90/10	0.04	11.5	60	99	3.9	...	...
90/10	0.04	12.5	66	100	4.4	...	...
90/10	0.04	14	65	98	1.85[d]	18.5	1.51
MUTUAL RECIPE AT 50° C.							
Butadiene/2-Cyano-2-propyl Acrylate							
90/10	0.114	14	50.5	97.6	2.1	...	...
90/10[e]	0.114	72	27	100	Very low	...	...
90/10	0.057	15	46.5[f]	95.2	2.3	...	...
90/10	0.076	8	49	100	1.2	...	...
90/10	0.076	12	81[f]	92.8	1.9	...	...
90/10	0.076	10	57	100	1.6[g]	12.4	1.25

[a] Composite figure for 20 polymerizations of 20 grams monomer charge combined and precipitated together for evaluation sample No. 310.

[b] Evaluation sample No. 260.

[c] Combination of 19 charges of 20 grams of monomer; evaluation sample No. 313.

[d] Composite sample of 20 runs; evaluation sample No. 267.

[e] Run made at 30° C.

[f] Considerable precoagulation in run.

[g] Composite of 19 charges of 20 grams of monomer; evaluation sample No. 314.

polymers. The other copolymers contained less than the total weight of monomer charged.

That a true copolymer was obtained rather than a mixture of polymers was demonstrated by the fractionation of the representative copolymers. Comparison of the nitrogen analyses of a gelled fraction of the copolymers with that of a gel-free fraction showed no difference in acrylate content.

The rate of polymerization of all cyanoalkyl acrylates in 90/10 charge ratios was greater than that of butadiene in every case. It was found that much more modifier was necessary in the recipes to obtain polymers 70 to 100% soluble in benzene than is necessary in butadiene polymerizations.

In the polymerization studies involving cyanomethyl and 2-cyano-2-propyl acrylates, it was found that yields differed markedly for the copolymers prepared from different samples of each acrylate, even though the samples possessed almost identical elemental analyses.

The 2-methyl-2-nitropropanol ester copolymerized with butadiene to give a satisfactory rubber (No. 267, Table V) from the standpoint of stress-strain values; its Gehman low temperature properties are better than for GR-S, but it has poor oil-resistance properties. 2-Cyanoethyl acrylate copolymerized with butadiene gave a rubber (No. 260, Table V) with fair tensile and good low temperature flexibility with a tendency to crystallize, but an oil resistance only slightly better than that of GR-S. The cyanomethyl acrylate copolymer gave a rubber (No. 313, Table V) with excellent oil resistance but poor low temperature flexibility.

The 1-cyanoethyl acrylate copolymer produced a high Mooney viscosity rubber (No. 310, Table V) which resulted in vulcanizates of high tensile strength values (4800 pounds per square inch). The low temperature flexibility is poor and the shape of the Gehman curve indicates that it would crystallize easily. At 77° F. it shows oil resistance only slightly inferior to that of Paracril 18-80 and at 180° F. it is the equal of Paracril in oil resistance.

The 2-cyano-2-propyl acrylate copolymer (No. 314, Table V) vulcanizate shows good tensile values, good resistance to crystallization, fair hysteresis-temperature rise but no improvement in oil resistance compared to GR-S. This last fact agrees with other results which we have noted in copolymers of cinnamic acid and cinnamonitrile and the acrylate of 2-methyl-2-nitropropanol where there appears to be steric hindrance around the nitrile, nitro, and carboxyl groups. Under these circumstances the group in question fails to introduce oil resistance.

MATERIALS

Phillips Petroleum Co. special purity butadiene was used. Goodrich Chemical Co. glacial acrylic acid was redistilled, and the fraction boiling at 39° to 40° C. at 8 mm., n_D^{20} 1.4211, was used. Eastman Kodak Co. practical grade acrylonitrile was dried over calcium chloride and redistilled. The fraction boiling at 77° to 77.5° C., n_D^{20} 1.3923, was used.

α-Methylene-δ-methyladiponitrile(I). An experimental sample was redistilled and the fraction of 127° to 129° C. (10 mm.), n_D^{20} 1.4530 was used.

Acrylyl Chloride. This was prepared from acrylic acid and thionyl chloride in about 76% yield. The material used had a boiling point of 73° to 75° C.

1-Cyanoethyl Acrylate(III). From 71 grams (1.0 mole) of lactonitrile, 10 grams of hydroquinone, 125 grams (1.05 moles) of redistilled dimethylaniline, and 90.5 grams (1.0 mole) of acrylyl chloride was obtained 70 grams of crude ester. To prevent extensive polymerization of the ester during distillation, special precautions were necessary.

A 200-ml. flask with ground-glass joint, Claisen head, thermometer, condenser, adapter for taking multiple fractions, and receivers was cleaned thoroughly with alcohol, chromic acid cleaning solution, water, distilled water, and redistilled water and dried in an oven. The crude ester was charged to the distilling flask, more hydroquinone was added as an inhibitor, and the remainder of the apparatus was assembled. The apparatus was swept with carbon dioxide for 0.5 hour and completely covered with towels to exclude all light. The receivers were immersed in acetone–dry ice baths and distillation at reduced pressure was carried out [boiling point 45° to 46° C. (2.5 mm.), n_D^{20} 1.4294]. The yield was 59.2 grams (47%).

	Analysis		
	C	H	N
Calcd. for $C_6H_7O_2N$	57.60	5.64	11.20
Found	57.64	5.55	11.02

2-Cyanoethyl Acrylate(V). In accordance with the general procedure of Rehberg for the preparation of *n*-butyl acrylate (*10*) there was placed in a 500-ml. flask 71 grams (1.0 mole) of 2-cyanoethyl alcohol, 258 grams (3.0 moles) of methyl acrylate, 3 grams of *p*-toluenesulfonic acid, and 5 grams of hydroquinone. A 50-cm. Vigreux column equipped with a partial–take-off head was put in place. The mixture was heated under reflux, and material boiling below 65° C. was removed about every hour; 55 ml. was collected during 20 hours. The excess methyl acrylate was then removed at atmospheric pressure by heating in an oil bath, and the residue was fractionally distilled under reduced pressure. Refractionation of this material from a small amount of hydroquinone produced 80 grams (63%) of 2-cyanoethyl acrylate, boiling point 67° to 68° C. (1.3 mm.), $n_D^{20.8}$ 1.4454.

Table V. Evaluation Samples of Copolymers and Terpolymers

	Butadiene/Acrylonitrile/Acrylic Acid (Azobisisobutyronitrile Recipe at 60° C. with 0.050 Gram Lauryl Mercaptan/20 Grams Monomers)				Butadiene/α-Methylene-δ-adiponitrile (Mutual Recipe at 50° C. with 0.050 Gram Lauryl Mercaptan/20 Grams Monomers)								Butadiene/Acrylonitrile/ α-Methylene-δ-adiponitrile (Mutual Recipe at 50° C. with 0.050 Gram Lauryl Mercaptan/20 Grams Monomers)				Butadiene/Acrylate (Cumene Hydroperoxide Recipe at 0° C.)				Butadiene/Acrylate (Mutual Recipe at 50° C.)
Illinois Sample No.	268	269	270	271	264	265	288	290[a]	292	293	294	295	259	287	289	291	2-Cyanoethyl 260	2-Methyl-2-nitropropyl 267	1-Cyanoethyl 310	Cyanomethyl 313	2-Cyano-2-propyl 314[a]
Monomer charge ratio	85.8/4.1/ 10.1	86.7/8.2/ 5.1	86.3/6.1/ 7.6	88.5/4.0/ 7.5	95/5	93/7	92/8	80/20	90/10	90/10	85/15	88/12	90/4/6	87/9/4	88/6/6	88/4/8	85/15	90/10	90/10	90/10	90/10
Time, hr.	8	8	8.8	11.3	5.75	5.25	5.25	4.5	5.25	5.25	5.25	5.25	5.25	4.92	4.75	4.67	15	6	14	6	10
Conversion, %	54	50	52	56	68	66	61	56	62	63	64	61	82.5	66	64	63	68.5	65	65	48	57
Combined monomer, %	6.6[b]; 4.4[c]	12.9[d]; 1.8[c]	10.4[e]; 2.2[c]	6.1[f]; 4.4[c]	6.8	9.2	10	28.9	12.6	12.8	16.9	15.1	...	...	...	...	10	16	18	25.5	12.4
Gel, %	12	3	7	12	...	...	14	5	32	30	15	28	...	72	56	29	...	10	20	43	4
Dilute solution viscosity	0.89	1.79	1.33	1.35	...	...	2.14	1.23	2.35	1.94	2.08	1.94	...	0.88	1.35	2.11	...	2.15	3.28	1.43	1.95
Mooney viscosity (ML-4 at 212° F.)	75	67	72	93	113	108.5	120	26	137	110	100	112	169	157	143	128	65	52	103	108	32
Williams plasticity[g]	0.169	0.164	0.161	0.185	0.210	0.202	0.214	0.103	0.190	0.202	0.196	0.208	0.252	0.240	0.223	0.219	...	...	...	...	...

[a] 0.075 gram lauryl mercaptan/20 grams monomer charged.
[b] Acrylonitrile calculated from 1.39% N in polymer.
[c] Acrylic acid estimated from oxygen content of polymer, which is determined by difference.
[d] Acrylonitrile calculated from 2.69% N in polymer.
[e] Acrylonitrile calculated from 2.17% N in polymer.
[f] Acrylonitrile calculated from 1.27% N in polymer.
[g] Load of 5000 grams on 2-ml. sample; 3-minute thickness at 212° F.

	Analysis C	H	N
Calcd. for $C_6H_7O_2N$	57.59	5.64	11.20
Found	57.64	5.65	10.94

Occasionally, for unknown reasons the material in the distilling flask polymerized during removal of excess methyl acrylate. This jellylike polymer was readily decomposed by heating at reduced pressure to produce the monomer which could be obtained pure by redistillation from hydroquinone and stored at 0° C. for extended periods without further spontaneous polymerization.

Cyanomethyl Acrylate (II). By utilizing the same precautions as described for the preparation of 2-cyanoethyl acrylate, 44.5 grams of cyanomethyl acrylate was prepared from 57 grams (1.0 mole) of glycolonitrile and 90.5 grams (1.0 mole) of acrylyl chloride, boiling point 28° to 29° C. (0.1 mm.), n_D^{20} 1.4374.

	Analysis C	H	N
Calcd. for $C_5H_5O_2N$	54.05	4.54	12.61
Found	54.20	4.81	12.33

2-Cyano-2-propyl Acrylate (IV). A much longer time of reaction was required for the preparation of this ester in yields comparable to those obtained in previous esterifications (19 hours as compared with 4 hours for previous esterifications). The ester was obtained in 50% yield from 85 grams (1.0 mole) of acetone cyanohydrin and 90.5 grams (1.0 mole) of acrylyl chloride, b.p. 33° to 34° C. (0.1 mm.), n_D^{20} 1.4280, yield 70 grams.

	Analysis C	H	N
Calcd. for $C_7H_9O_2N$	60.43	6.53	10.07
Found	60.04	6.72	10.07

2-Methyl-2-nitropropyl Acrylate (VI). The synthesis of 2-methyl-2-nitropropyl acrylate was also attempted according to the method of Rehberg (*10*), but only a 25% yield of impure ester was obtained.

2-Methyl-2-nitropropanol was esterified with acrylyl chloride by the esterification method of Hauser and coworkers (*6*), and the ester was obtained in 60% yield. It is a colorless liquid boiling at 53° C. (0.4 mm.), n_D^{19} 1.4480. The pure compound does not appear to polymerize after being stored at 0° C. for 1 year.

	Analysis C	H	N
Calcd. for $C_7H_{11}NO_4$	48.55	6.40	8.09
Found	48.59	6.25	8.25

POLYMERIZATIONS

Butadiene, Acrylic Acid, and Acrylonitrile Terpolymers. The usual 4-ounce screw-cap bottles fitted with self-sealing gaskets were charged in a standard manner with the following: azobisisobutyronitrile, 60 mg.; redistilled water, boiled and cooled under nitrogen, 40 ml.; MP-635-S, 2 ml.; acrylonitrile, variable; modifier, variable; butadiene, variable (the bottle was charged with an excess; the excess was allowed to evaporate and the bottle was then capped); acrylic acid, variable, and added to the charge by injection through the cap by means of a hypodermic needle.

MP-635-S has the following composition: sodium alkane sulfonate (C_{16} range), 49.5%; unreacted hydrocarbon, 10.2%; sodium chloride, 0.86%; sodium sulfate, 0.4%; isopropyl alcohol, 3%; and water to make 100%.

Hooker Electrochemical Co. technical lauryl mercaptan, boiling point 115° to 117° C. (5 mm.), average molecular weight 210.7, average formula $C_{12.6}H_{26.2}SH$, was used as modifier for all polymerizations described in this paper.

The charged bottles were rotated end over end in a constant temperature bath (60° C.) for the indicated time and the polymers were isolated by coagulation with 25 ml. of alum solution (1 part of alum, 10 parts of water, and 1.1 parts of concentrated

Table VI. Stress-Strain Data at 77° F. for Butadiene-Acrylonitrile–Acrylic Acid Terpolymers

(Tread-type recipe)

Min. Cured at 292° F.	X-603[a]	Illinois Sample No. 268	269	270	271
		300% Modulus, Lb./Sq. Inch			
25	540	1370	1260	1550	1320
50	1270	2080	1900	2400	2100
100	1920	2740	...	...	...
		Tensile Strength, Lb./Sq. Inch			
25	2030	3240	2480	3300	2830
50	4010	3130	2500	3160	2740
100	4030	2910	2060	2630	2780
		Elongation, %			
25	700	460	440	450	440
50	620	380	350	350	340
100	480	310	280	290	290

[a] GR-S prepared at 47° C. in mutual recipe; butadiene/styrene ratio of 71/29; contained 2% gel; Mooney viscosity (ML-4 212° F.) = 53; dilute solution viscosity = 2.4.

Table VII. Low Temperature Properties of Butadiene-Acrylonitrile–Acrylic Acid Terpolymers

(Tread-type recipe)

	Natural Rubber	X-603	Illinois Sample No. 268	269	270	271
Min. cured at 292° F.	...	60	50	50	50	50
		GEHMAN LOW TEMPERATURE DATA				
		Temperature[a], ° C.				
T_2	...	−26	−12.5	−16	−15	−14
T_5	...	−43	−44	−42	−42.5	−48
T_{10}	...	−45	−50	−46	−47.5	−53.5
T_{100}	...	−50	−59	−52.5	−54	−63
Freeze point	...	−51	−57.5	−52.5	−56	−63
Gage, inch	...	0.082	0.082	0.087	0.087	0.092
		TEMPERATURE RETRACTION TEST[b]				
Retraction, %		Temperature, ° C.				
5	−60	−55	−60	−51	−58	−63
10	−54	−53	−55	−50	−55	−58
20	−46	−50	−48	−49	−51	−55
30	−35	−49	−42	−48	−48	−50
40	−27	−48	−35	−43	−41	−43
50	−24	−44	−28	−38	−33	−35
60	−21	−41	−24	−32	−28	−31
70	−18	−37	−20	−25	−20	−25
80	−15	−32	−12	−20	−16	−20
90	− 9	−21	− 0	− 7	− 4	− 7
Difference TR-10 and TR-70	36	16	35	25	35	33

[a] Temperatures at which relative rotation stiffness is met.
[b] 250% elongation.

Table VIII. Oil Resistance of Butadiene-Acrylonitrile–Acrylic Acid Terpolymers

(77° F., 7-day immersion)

	Perbunan 18	X-603	Illinois Sample No. 268	269	270	271
Min. cured at 292° F.	..	60	50	50	50	50
			% Swell by Volume			
No. 1 oil	0	9	6	6	3	3
No. 2 oil	6	26	13	13	13	19
No. 3 oil	19	100	52	52	52	64
100% iso-octane	13	56	33	33	30	44
60/40 iso-octane/toluene	82	174	100	100	110	135
Special solvent[a]	77	174	95	95	120	130

[a] 15% xylene, 20% toluene, 5% benzene, and 60% iso-octane.

Table IX. Physical Properties of Butadiene-Acrylonitrile–Acrylic Acid Terpolymers

(Carcass-type recipe)

Min. Cured at 280° F.	X-603	Illinois Sample No. 268	269	270	271
	STRESS-STRAIN DATA AT 77° F.				
		300% Modulus, Lb./Sq. Inch			
20	210	550	740	620	720
40	560	700	840	800	930
80	830	700	720	710	900
		Tensile Strength, Lb./Sq. Inch			
20	1770	1330	1540	1280	1290
40	2000	1300	1470	1330	1260
80	1560	1210	1350	1190	1170
		Elongation, %			
20	920	560	530	530	440
40	620	450	440	430	370
80	450	410	430	400	370
	GOODRICH HYSTERESIS DATA AT 212° F.				
		Shore Hardness			
30	41[a]	40	40	41	43
60	42[b]	40	41	40	43
90	43[c]	41	40	41	43
		Initial Compression, %			
30	32.0[a]	43.1	41.7	41.9	37.0
60	29.8[b]	39.1	40.6	39.6	33.1
90	29.1[c]	38.7	39.8	38.6	35.0
		Temperature Rise, ° F.			
30	23[a]	73	61	71	49
60	18[b]	36	39	38	34
90	18[c]	32	36	38	53
		Final Temperature Rise[d], ° F.			
30	28 (30)[a]	73 (10)	74 (16)	75 (12)	67 (19)
60	23 (30)[b]	65 (25)	52 (18)	73 (23)	58 (35)
90	22 (30)[c]	62 (20)	71 (18)	75 (25)	84 (15)
		Set, %			
30	15.3[a]	...	...	...	...
60	8.6[b]	...	...	...	...
90	6.0[c]	...	...	...	...

[a] Cured 60 min. at 280° F.
[b] Cured 90 min. at 280° F.
[c] Cured 120 min. at 280° F.
[d] Figure in parenthesis is total time of test, min.

hydrochloric acid by weight), followed by 50 ml. of methanol for each 20 grams of monomer charge.

The experiments carried out to test the feasibility of the preparation of these terpolymers are recorded in Table I and the evaluation samples are described in Table V.

Copolymers and Terpolymers of α-Methylene-δ-methyladiponitrile. The products described in Tables II, III, and V were prepared in the standard 4-ounce screw-cap bottles using a 20-gram monomer mixture charge with 35 grams of a 2.86% solution of a sodium fatty acid soap (Office of Synthetic Rubber specifications), 2.0 ml. of a freshly prepared 3.0% solution of potassium persulfate as initiator, and technical lauryl mercaptan as modifier in amounts indicated in the tables. After end over end tumbling at 50° C. for the appropriate time, phenyl-β-naphthylamine was added as an emulsion in soap, and the polymer was isolated by the addition of a salt-acid coagulant (a 4.2% sulfuric acid solution saturated with sodium chloride).

These copolymers and terpolymers were all prepared in the mutual recipe (*11*) at 50° C.

Copolymers of Cyano and Nitro Alkyl Acrylates with Butadiene. Because of the tendency of these monomers to homopolymerize rapidly in the soap solution before the remaining ingredients could be added, a special technique was developed for effecting the polymerizations.

The polymerizations were carried out in 4-ounce screw-cap bottles equipped with self-sealing rubber gaskets. In the cumene hydroperoxide recipe (*13*), the activator was injected into the

Table X. Stress-Strain Data at 77° F. for α-Methylene-δ-methyladiponitrile Copolymers and Terpolymers

(Tread-type recipe)

Min. Cured at 292° F.	X-720[a]	Illinois Sample Number 259	264	265	287	288	289	290	291	292	293	294	295
						300% Modulus, Lb./Sq. Inch							
25	350	...	...	...	1590[b]	950[b]	1100[b]	710	1890	800[b]	1700	1270	1130
50	790	...	...	...	2090	1220	1510	1210	2680	1370	2440	2050	1840
100	1280	...	...	...	2310	1440	1830	1390	3060	1490	2820	2370	2300
						Tensile Strength, Lb./Sq. Inch							
25	2260	2370	2190	2450	3100	3550	3800	1690	3970	4090	4140	4110	4020
50	3610	2490	2050	2300	2830	2930	2920	2430	3630	3030	3140	3620	3580
100	3960	2270	2090	2000	2660	2600	2900	1870	3000	2390	2980	3050	2500
						Elongation, %							
25	890	230	270	290	320	470	420	530	470	530	530	600	600
50	710	180	200	240	240	340	290	480	370	320	350	420	440
100	590	140	200	170	230	270	270	360	300	260	310	360	340

[a] GR-S sample prepared in mutual recipe at 50° C. to 68% conversion; butadiene/styrene ratio is 71/29 and Mooney viscosity (ML4-212° F.) is 48.

[b] 200% modulus.

bottle through a hole in the cap by means of a small hypodermic syringe after all the other ingredients had been added. In these experiments the exact recipe used was 32 grams of 3.1% aqueous potassium laurate solution buffered to pH 9.6 with potassium carbonate; 0.05 gram of 71.9% cumene hydroperoxide; variable amount of Hooker's lauryl mercaptan; 20 grams of monomers; and 4 ml. of activator solution (made with 2.7 grams of potassium pyrophosphate and 3.24 grams of ferrous sulfate heptahydrate in 45 ml. of distilled water).

In the mutual recipe (*14*), all the ingredients except the ester were added in the conventional order. Just as the excess butadiene was boiling out of the polymerization bottle, the acrylate was quickly added from a small vial in which the proper amount of ester has previously been weighed and stored at −55° C. until needed. The polymerization bottle was sealed and tumbled at the desired temperature. In the cumene hydroperoxide recipe, the potassium laurate solution was weighed into the polymerization bottles; the bottles were sealed and cooled to about 5° C., opened, and the cumene hydroperoxide and mercaptan were quickly added. The butadiene and then the ester from its individual vial were added as for the mutual recipe (*14*); the bottles were sealed, injected with activator, and tumbled at 0° C. for the desired length of time. The polymer was coagulated by the addition of 25 ml. of salt-acid coagulant to the emulsion for a 20-gram monomer charge. Some typical experiments are described in Table IV.

The copolymer of butadiene and the acrylate of 2-methyl-2-nitropropanol was made in the standard cumene hydroperoxide recipe. A few typical copolymerizations are described in Table IV.

The copolymers of butadiene and 2-cyano-2-propyl acrylate were not readily formed in the cumene hydroperoxide recipe at 0° C. but were formed in the Mutual recipe at 30° and 50° C. Some typical experiments are recorded in Table IV. The evaluation samples of acrylate copolymers are listed in Table V.

EVALUATION OF POLYMERS

The new polymers have been compounded and cured in the following tread-type and carcass stock recipes.

Tread-Type Recipe	Parts
Polymer	100
EPC black	40
Zinc oxide	5
Sulfur	2
Benzothiazole disulfide	1.75
Total	148.75

Carcass-Type Recipe	Parts
Polymer	100
Statex 93	30
Red lead	2.5
Sulfur	2
Benzothiazole disulfide	1
Circosol-2XH	20
Total	155.5

Table XI. Low Temperature Properties of α-Methylene-δ-methyladiponitrile Copolymers and Terpolymers

(Tread-type recipe; samples cured 50 min. at 292° F.)

	X-672	Perbunan 18	Illinois Sample Number 259	264	265	287	288	289	290	291	292	293	294	295
						GEHMAN LOW TEMPERATURE DATA								
						Temperature, ° C.								
T_2	−30	..	−40.5	−46	−36.5	−27.5	−29.5	−28.5	0	−24.5	−27	−22.5	−15	−15
T_5	−43	..	−49.5	−57	−45.5	−33	−39	−34.5	−10	−31	−36	−31	−23	−24.5
T_{10}	−46	..	−53.5	−61	−51	−36	−45	−38	−13	−34	−41.5	−35.5	−27	−29
T_{100}	−52	..	−65.5	−70	−65.5	−47.5	−62.5	−48.5	−25	−49	−60.5	−56	−48.5	−50
Freeze point	−53	..	−60.5	−68.5	−63	−42	−56	−44	−21.5	−40.5	−52	−45	−36.5	−38
Gage, inch	0.074	..	0.095	0.086	0.080	0.082	0.084	0.090	0.078	0.093	0.085	0.086	0.080	0.080
						OIL RESISTANCE (77° F., 7-DAY IMMERSION)								
						% Swell by Volume								
No. 1 oil	..	0	3	9	9	3	9	0	0	3	13	6	3	6
No. 2 oil	..	6	16	26	16	6	19	6	3	13	19	16	13	16
No. 3 oil	..	19	52	64	56	26	69	37	13	41	73	52	52	52
100% iso-octane	..	13	33	41	33	19	41	26	16	37	44	37	33	41
60/40 iso-octane/toluene	..	82	91	100	95	86	110	86	77	105	135	120	115	120
Special solvent mixture[a]	..	77	91	100	95	82	110	91	73	105	130	115	110	125

[a] 15% xylene, 20% toluene, 5% benzene, 60% iso-octane.

Table XII. Physical Properties of α-Methylene-δ-methyladiponitrile Copolymers and Terpolymers

(Carcass-type recipe)

Min. Cured at 280° F.	X-720	Illinois Sample Number											
		259	264	265	287	288	289	290	291	292	293	294	295
STRESS-STRAIN DATA AT 77° F.													
300% Modulus, Lb./Sq. Inch													
20	120	630	730	660	900	610	760	80	570	460	410	380	420
40	390	820	1020	890	1370	960	1190	270	950	770	670	620	650
80	630	1010	...	...	...	...	...	370	1070	920	830	720	800
Tensile Strength, Lb./Sq. Inch													
20	1590	1070	1260	1310	1720	1330	1610	1160	1910	2160	1750	2120	1940
40	1870	1140	1130	1090	1670	1080	1530	1740	1450	1340	1330	1600	1580
80	1210	1100	1000	890	1170	890	1140	1080	1230	1390	1150	1600	1300
Elongation, %													
20	1060	290	420	450	490	490	520	1200	620	700	670	800	730
40	700	260	320	340	360	330	350	840	380	420	430	540	560
80	430	210	260	260	250	270	270	560	320	370	370	500	400
GOODRICH HYSTERESIS DATA AT 212° F.													
Shore Hardness													
30	41[a]	58	49	51	49	46	49	35	46	45	43	41	44
60	41[b]	58	52	51	50	48	49	38	49	47	44	44	45
90	41[c]	57	52	52	51	50	50	39	48	48	46	45	45
Initial Compression, %													
30	32.7[a]	20.9	27.7	27.4	26.0	28.5	27.4	51.2	29.2	31.1	31.4	34.5	33.3
60	32.3[b]	19.5	24.6	25	24.8	26.4	25.3	42.2	26.3	27.0	28.4	32	29.4
90	31.3[c]	18.3	23.3	25.9	23.3	24.3	24.3	42.5	25.4	26.5	28.0	31.2	29.3
Temperature Rise, ° F.													
30	34[a]	20	23	22	22	22	23	...	24	28	24	33	24
60	25[b]	21	21	17	18	18	18	48	20	22	18	21	17
90	23[c]	19	20	16	16	18	17	61	14	19	15	20	15
Set, %													
30	16.6[a]	8.5	11.5	11	8.6	11.5	11.0	..[d]	12.6	16.6	13.4	20.0	14.5
60	6.3[b]	3.7	4.6	4.4	3.0	3.9	3.3	...	3.7	4.5	4.3	7.3	5.0
90	5.0[c]	2.4	3.4	2.5	2.3	2.4	2.5	...	2.6	2.5	2.8	5.2	3.2

[a] Cured 60 min. at 280° F.
[b] Cured 90 min. at 280° F.
[c] Cured 120 min. at 280° F.
[d] Pellets slipped out of testing machine either at start or during test.

The results of the evaluation of the butadiene-acrylonitrile-acrylic acid terpolymers are listed in Tables VI to IX; those on the copolymers and terpolymers of α-methylene-δ-methyladiponitrile are listed in Tables X to XII. The evaluation of the nitro- and cyanoalkyl acrylate copolymers are listed in Tables XIII to XVII.

DISCUSSION OF RESULTS

The vulcanizates of the terpolymers of butadiene with acrylic acid and acrylonitrile when compounded and cured have much better oil-resistance properties than those of GR-S but they are not equal to those of Perbunan 18. Some of the terpolymers have much better low temperature properties than GR-S and, consequently, are superior in this respect to Perbunan 18; yet their oil-resistance is not good enough for practical use.

The copolymers of butadiene with α-methylene-δ-methyladiponitrile show an increase in oil resistance with increased nitrile content, but concurrent with this there is a decrease in the freeze resistance. It is possible to adjust the proportion of the two monomers to achieve fair oil resistance and fair low temperature properties (Nos. 259, 264, and 265).

The various cyanoalkyl acrylate ester copolymers with butadiene show oil resistance and freeze points very much like those of an acrylonitrile copolymer of the same nitrogen content except in the case of 2-cyano-2-propyl acrylate. The copolymer (No. 314) made from charges of 2-cyano-2-propyl acrylate (10)–butadiene (90) has very good low temperature properties and fair stress-strain properties but no oil resistance. Presumably this lack of oil resistance may be related to steric factors which result in shielding of the cyano group. Similar lack of oil resistance was observed in the case of the copolymer of butadiene and the acrylate of 2-methyl-2-nitropropyl acrylate. It has also been noted (*9*) that copolymers of butadiene and cinnamic acid and of butadiene and cinnamonitrile are lacking in oil resistance.

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Table XIII. Stress-Strain Data at 77° F. for Nitro and Cyanoalkyl Acrylate Copolymers

(Tread-type recipe)

Min. Cured at 292° F.	X-720	Illinois Sample No.				
		260	267	310	313	314
300% Modulus, Lb./Sq. Inch						
25	520	1380	950	1740	2950	580
50	1010	2160	1610	2460	3650	1310
100	1480	2470	1990	2940	...	1790
Tensile Strength, Lb./Sq. Inch						
25	2540	3220	3890	4880	4600	3310
50	3860	2760	3680	4690	4270	3030
100	3980	2590	3430	4890	3600	2580
Elongation, %						
25	770	460	630	530	410	770
50	650	350	480	440	340	510
100	530	310	410	400	230	380

Table XIV. Low Temperature Properties of Nitro and Cyanoalkyl Acrylate Copolymers

(Tread-type recipe; cured 50 min. at 292° F.)

	X-720	Illinois Sample No. 260	267	310	313	314
GEHMAN LOW TEMPERATURE DATA						
	Temperature, ° C.					
T_2	−27.5	−28	−27.5	−11	+10.5	−34
T_5	−42.5	−44	−46	−26	− 8.0	−49.5
T_{10}	−45.5	−51	−50	−30	−20.0	−52
T_{100}	−52	−65	−57.5	−48	−60.0	−61.5
Freeze point	−53.5	−66	−57.5	−37	−40.0	−57.5
Gage, inch	0.090	0.083	0.082	0.077	0.097	0.085
TEMPERATURE RETRACTION TEST[a]						
Retraction, %	Temperature, ° C.					
5	−55	−57	−58	...	−36	−65
10	−53	−53	−53	...	−26	−61
20	−51	−48	−51	...	−18	−58
30	−48	−41	−48	...	−12	−54
40	−44	−37	−45	...	− 8	−52
50	−42	−33	−41	...	− 3	−49
60	−38	−29	−37	...	+ 3	−44
70	−34	−25	−33	...	+ 8	−40
80	−27	−21	−28	...	+14	−31
90	−19	−13	−18	...	+23	−21
Difference between TR-10 and TR-70	19	28	20		34	21

[a] 100% elongation.

Table XV. Oil Resistance of Cyanoalkyl Acrylate Copolymers

(77° F., 7-day immersion; cured 50 min. at 292° F.)

	Perbunan 18	X-720	Illinois Sample No. 260	267	310	313	314
	% Swell by Volume						
No. 1 oil	0	23	30	30	0	9	19
No. 2 oil	6	41	82	91	6	16	41
No. 3 oil	19	135	52	52	33	33	115
Iso-octane	13	86	146	157	26	33	73
60/40 iso-octane/toluene	82	238	146	157	86	91	192
Special solvent[a]	77	238	..	..	91	86	192

[a] 15% xylene, 20% toluene, 5% benzene, and 60% iso-octane.

Table XVI. Physical Properties of Cyanoalkyl Acrylate Copolymers

(Carcass-type recipe)

Min. Cured at 280° F.	X-720	Illinois Sample No. 260	267	313	314
STRESS-STRAIN DATA AT 77° F.					
	300% Modulus, Lb./Sq. Inch				
20	110	220	100	110	85
40	390	420	330	300	280
80	660	700	510	440	430
	Tensile Strength, Lb./Sq. Inch				
20	1850	1420	1910	2170	1310
40	2040	1470	1590	2030	950
80	1380	870	1310	1720	800
	Elongation, %				
20	990	730	1020	1010	930
40	700	530	680	730	540
80	440	830	530	590	410
GOODRICH HYSTERESIS DATA AT 212° F.					
	Shore Hardness				
30	42[a]	43	39	38	35
60	43[b]	45	41	38	36
90	43[c]	46	41	38	37
	Initial Compression, %				
30	31.9[a]	34.7	37.5	40.2	43.4
60	30.0[b]	31.1	31.2	34.9	35.8
90	28.8[c]	29.9	31.7	34.3	35.2
	Temperature Rise, ° F.				
30	30[a]	42	41	42	...
60	25[b]	26	22	27	28
90	24[c]	20	20	22	21
	Set, %				
30	17.9[a]	25.9	31.6	31.3	...
60	8.7[b]	10	9.7	11.5	16.8
90	6.1[c]	4.8	6.1	7.3	8.7

[a] Cured 60 min. at 280° F.
[b] Cured 90 min. at 280° F.
[c] Cured 120 min. at 280° F.

Table XVII. Oil Resistance of 1-Cyanoethyl Acrylate-Butadiene Copolymers

(Cured 50 min. at 292° F.; 7-day immersion)

	Test Temp., 77° F.		Test Temp., 140° F.		Test Temp., 180° F.	
	Par. 18-80	Illinois Sample No. 310	Par. 18-80	Illinois Sample No. 310	Par. 18-80	Illinois Sample No. 310
	% Swell by Volume					
No. 1 oil	0	0	9	10	13	13
No. 2 oil	0	6	23	30	16	33
No. 3 oil	19	33	44	60	52	60
100% iso-octane	16	26	33	33	30	33
60/40 iso-octane/toluene	82	86	100	100	100	100
Special solvent[a]	82	91	95	95	105	100

[a] 15% xylene, 20% toluene, 5% benzene, and 60% iso-octane.

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