BLENDS OF CIS-POLYBUTADIENE WITH NITRILE RUBBER

PART 1

The butadiene-acrylonitrile copolymers find wide application in various seals and gaskets and other parts, which are in constant contact with oil. In such service, the oil sometimes tends to extract plasticizer and cause shrinkage which might destroy the seal. To offset this effect, it is common practice to blend a little SBR with the NBR.

In this study, it is shown that Ameripol CB can also be blended with NBR to compensate for shrinkage. In addition, a better ratio of low-temperature flexibility to oil-swell can be obtained from a blend of Ameripol CB and NBR than from a similar blend of SBR and NBR.

To demonstrate this phenomenon, a compound based on a blend of Hycar 1052 and Ameripol CB 220, having the same degree of oil-swell as a Hycar 1052/SBR 1502 blend, exhibits a considerably lower brittleness temperature. Specifically, an 80/20 blend of Hycar 1052/Ameripol CB 220 has the same resistance to oil swell as a 75/25 blend of Hycar 1052/SBR 1502, but with better impact resistance at lower temperature. Other physical properties are comparable except for abrasion resistance which is better for blends containing Ameripol CB.

In conducting this study, all compounds were mill-mixed according to a standard milling procedure. The Hycar 1052 was first milled to produce a rolling bank, then the Ameripol CB or SBR 1502 was added and blended thoroughly. Compounding ingredients were then added in the usual manner. Subsequent testing was done in accordance with ASTM standards.

The first comparisons were made on the basis of equal ratios of nitrile rubber to non-nitrile rubber. See compounds No. 1 and 2, Table 1, based on 75/25 ratios of nitrile to non-nitrile. When comparing 75/25 blends of Hycar with SBR or Ameripol CB, the Hycar/CB blend showed the lower brittleness temperature, only seven test specimens out of ten having failed at −100°F, the lowest attainable temperature with the equipment used for these studies. The Hycar/SBR compound had a brittleness temperature (T_b) value of −75°F.

Part 2 of this report shows SBR to have somewhat greater resistance to oil-swell than Ameripol CB, therefore it was not surprising to find that the 75/25 blend of Hycar/CB produced a greater volume swell in ASTM Oils #1 and #3 than did the 75/25 blend of Hycar/SBR.

For this reason, it was decided that the blends could be more correctly compared on the basis of equal oil resistance. Compound No. 3 based on an 80/20 blend of Hycar/CB was found to have the same oil resistance as Compound No. 1 based on a 75/25 blend of Hycar/SBR. In this case, as in the comparison of the first two compounds, the brittleness temperature of the Hycar/CB blend was superior. Only nine out of ten test specimens failed at −100°F so that again, T_b could not accurately be determined.

In comparing Compounds No. 1 and 3 it is obvious, except for low-temperature brittleness and a three-fold increase in abrasion resistance, that there is considerable similarity in other properties.

RESISTANCE OF VARIOUS RUBBER VULCANIZATES TO SOLVENTS AND OILS

PART 2

Data are presented in this report which show the volume and weight changes which occur when six different rubber vulcanizates are immersed in thirteen different solvents and oils at room temperature for one, three and seven days.

THE RUBBERS SELECTED FOR THE STUDY ARE:

Cis-polybutadiene (98% cis content) .. **Ameripol CB 220**
Styrene-butadiene rubber, SBR .... **Ameripol 1500**
Natural rubber, NR .... **#1 RSS**
Isobutylene-isoprene rubber, IIR .... **Butyl 150**
Chloroprene rubber, CR .... **Neoprene GNA**
Butadiene-acrylonitrile (High nitrile), NBR .. **Hycar 1001**

THE IMMERSION FLUIDS SELECTED INCLUDE SEVERAL COMMON CHEMICAL GROUPS:

Aliphatic hydrocarbons .... **N-Hexane**
Chlorinated aliphatics .... **Ethylene dichloride**
Nitro aliphatics .... **Nitropropane**
Aromatic hydrocarbons .... **Benzol**
Chlorinated aromatics .... **Monochlorobenzol**
Ethers .... **Isopropyl ether**
Esters .... **Ethyl acetate**
Alcohols .... **Ethanol**
Ketones .... **Methyl ethyl ketone, acetone**
Terpenes .... **Turpentine**
Oils .... **Cottonseed oil, mineral oil**

The compounds chosen for this study are of the mechanical goods type and were selected on the basis of equal pigment loading and equal plasticizer content rather than on physical properties in order to minimize compounding variables which might influence volume changes. See Table 2.

The volume and weight changes reported here may be considered typical for compounds containing 80 phr of carbon black and 14 to 16 parts of softeners and plasticizers which might be extracted by some of the solvents. A volume swell is a measure of the sum of solvent swelling action and plasticizer loss, if any. A negative value, therefore, would, of course, indicate low or zero swell and plasticizer loss. See Tables 3 and 4.

In interpreting the data it should be kept in mind that a higher pigment loading would reduce swell and a lower plasticizer content would reduce shrinkage. By the same token, temperature variations and testing under dynamic rather than static conditions can, also, exert significant effect. Also, mixtures of solvents can have a substantially different effect than can be predicted from the actions of the solvents taken separately. Another weakness in volume swell data is that it cannot safely be considered to indicate changes in other physical properties.

In short, the only truly reliable criterion for predicting the suitability of any rubber compound for a specific application is to test its performance under actual service conditions. It is believed, however, that these volume change data, judiciously interpreted, will assist the product engineer and compounder in selecting the proper rubber for a given product application.

For example:

1. Ameripol CB and natural rubber have almost equal resistance to swell in the fluids selected for this study.
2. SBR 1500 shows a little better oil resistance than Ameripol CB or natural rubber.
3. Butyl rubber shows greater resistance to the ketones and ethyl acetate than the general purpose rubbers, SBR and NR.
4. Neoprene and Hycar, as expected, show superior oil and aliphatic hydrocarbon resistance.

For the solvent action on **unvulcanized** rubbers see Technical Data Report No. 5 and previously published articles.[1]

1. "Solubility and Adhesion of Ameripol CB", D. V. Sarbach, Rubber World, November, 1962, p. 74.
"Solubility of Unvulcanized Rubbers", D. V. Sarbach and B. S. Garvey, Rubber World, March, 1947.

TABLE 1

RECIPE	1	2	3
Hycar 1052	75	75	80
Ameripol 1502, SBR	25	—	—
Ameripol CB 220	—	25	20
Zinc oxide	5	5	5
Stearic acid	1	1	1
FEF Black (1)	40	40	40
Tetramethyl thiuram disulfide (2)	3.5	3.5	3.5
	149.5	149.5	149.5
MOONEY SCORCH AT 250°F. — LARGE ROTOR			
Minimum Mooney	54	56.5	55
Mooney at 4 minutes	55	57.5	56.5
Scorch time (Δ5) (minutes)	9¾	9½	9
Cure time (Δ30) (minutes)	14	13¼	13½
ORIGINAL PROPERTIES — ALL CURES AT 338°F.			
MODULUS AT 300% ELONGATION (psi)			
Minutes cured — 5	1190	1080	1080
10	1230	1260	1290
20	1340	1340	1340
ULTIMATE TENSILE STRENGTH (psi)			
Minutes cured — 5	2260	1640	2060
10	2350	1840	2210
20	2330	1870	2320
ULTIMATE ELONGATION (%)			
Minutes cured — 5	540	450	590
10	510	410	510
20	480	400	510
HARDNESS (DURO A)			
Minutes cured — 5	65	60	59
10	65	62	60
20	65	62	60
COMPRESSION SET — ASTM METHOD B*			
70 hrs. at 212°F. (%)	20	25	26
ASTM D 1630-59-T ABRASION INDEX*	130	453	453
LOW TEMPERATURE BRITTLENESS — ASTM D 746			
Pass (°F.)	−70	−80	−80
Fail (°F.)	−75	−85	−85
T_b (°F.)	−75	**	***
IMMERSIONS — SAMPLES CURED 10 MINUTES AT 338°F.			
ASTM Oil #1 aged 70 hrs. at 212°F.			
Ultimate tensile strength (psi)	2300	1750	2240
Tensile change (%)	−2	−5	+1
Ultimate elongation (%)	430	350	450
Elongation change (%)	−16	−15	−12
Hardness (Duro A)	57	52	54
Hardness change (points)	−8	−10	−6
Volume change (%)	+9	+19	+9
ASTM Oil #3 aged 70 hrs. at 212°F.			
Ultimate tensile strength (psi)	1550	1140	1420
Tensile change (%)	−34	−38	−36
Ultimate elongation (%)	330	270	350
Elongation change (%)	−35	−34	−31
Hardness (Duro A)	39	37	42
Hardness change (points)	−26	−25	−18
Volume change (%)	+57	+71	+55
Air test tube aged 70 hrs. at 250°F.			
Ultimate tensile strength (psi)	2380	1970	2420
Tensile change (%)	+1	+7	+10
Ultimate elongation (%)	360	320	390
Elongation change (%)	−29	−22	−24
Hardness (Duro A)	70	67	66
Hardness change (points)	+5	+5	+6

*Test specimens cured 20 min. @ 338°F.

**Seven out of ten T-50 specimens failed at −100°F.

***Nine out of ten T-50 specimens failed at −100°F.

(1) Philblack A, Phillips Chemical Co.

(2) Methyl Tuads, R. T. Vanderbilt Co., Inc.

COMPOUNDS USED TABLE 2

Cis-Polybutadiene		SBR		NR	
Ameripol CB 220	100.0	Ameripol 1500	100.0	#1RSS Plasticated	100.0
Stearic/Palmitic acid[1]	4.0	Stearic acid	2.0	Stearic acid	3.0
Zinc oxide	5.0	Zinc oxide	5.0	Zinc oxide	5.0
N-Isopropyl-N'-phenyl-p-phenylenediamine[2]	1.0	Phenyl-beta-naphthylamine[7]	1.0	Mixture of octylated diphenyl amines[8]	1.0
Modified Phenolic resin[3]	3.0			Polymerized petroleum H.C.[9]	7.0
Naphthenic oil[4]	8.0	Naphthenic oil	14.0	Naphthenic oil	7.0
Tetramethyl thiuram disulfied[5]	.1	Tetramethyl thiuram disulfide[5]	.4		
Sulfur	1.5	Sulfur	2.0	Sulfur	2.75
N-cyclohexyl-2-benzothiazole sulfenamide[6]	1.0	N-cyclohexyl-2-benzothiazole sulfenamide	1.5	Benzothiazyl disulfide[10]	1.0
SRF black	80.0	SRF black	80.0	SRF black	80.0
TOTAL	203.6		205.9		206.75
Sp. Gr.	1.17		1.19		1.18
ML-4 @ 212°F.	53		54		40
Optimum Cure @ 307°F., min.	15-20		10-15		15-20
Tensile strength (psi)	2100		2550		2550
200% Modulus (psi)	*1200*		*1800*		*1000*
Elongation (%)	350		350		500
Shore A-2 hardness	62		68		65

1. Groco 50D, The A. Gross Co.
2. Flexzone 3C, Naugatuck Chemical Division, U.S. Rubber Co.
3. Catalin Tackifying Resin 8318, Catalin Corporation of America
4. Gulf Oil 566, Gulf Oil Corporation
5. Methyl Tuads, R. T. Vanderbilt Co.
6. Santocure, Monsanto Chemical Co.
7. AgeRite Powder, R. T. Vanderbilt Co.
8. AgeRite Stalite, R. T. Vanderbilt Co.
9. Paraflux 2016, The C. P. Hall Co.
10. Altax, R. T. Vanderbilt Co.

IIR		CR		NBR	
Butyl 150	100.0	Neoprene GNA	100.0	Hycar 1001	100.0
Stearic acid	2.0	Stearic acid	.5	Stearic acid	1.0
Zinc oxide	5.0	Zinc oxide	5.0	Zinc oxide	5.0
Naphthenic oil	14.0	Phenyl-beta-naphthylamine	1.0	Dioctyl phthalate[13]	14.0
Tetramethyl thiuram disulfide	1.5	Polymerized petroleum H.C.	7.0	Tetramethyl thiuram disulfide	.25
Sulfur	1.25	Aromatic oil	7.0	Sulfur	1.5
2-Mercaptobenzothiazole[11]	1.00	Light calcined magnesia[12]	4.0	Benzothiazyl disulfide	1.5
SRF black	80.0	SRF black	80.0	SRF black	80.0
TOTAL	204.75		204.50		203.25
Sp. Gr.	1.17		1.42		1.29
ML-4 @ 212°F.	38		51		86.5
Optimum Cure @ 307°F., min.	25-30		10-15		10-15
Tensile strength (psi)	1200		2200		2800
200% Modulus (psi)	380		1550		2500
Elongation (%)	690		400		250
Shore A-2 hardness	65		74		71

11. Captax, R. T. Vanderbilt Co.
12. Maglite D, The C. P. Hall Co.
13. Good-rite GP 261, B. F. Goodrich Chemical Co.

TABLE 3 IMMERSION VALUES

Solvent	Ethylene Dichloride			Acetone			Methylethyl Ketone			Ethanol			Benzol			Chlorobenzol			Isopropyl Ether		
Days at Room Temperature	1	3	7	1	3	7	1	3	7	1	3	7	1	3	7	1	3	7	1	3	7
Volume Change, Percent																					
Ameripol CB	130	119	110	8	7	7	39	35	36	−2	−4	−4	199	186	199	219	219	219	67	66	65
SBR	103	99	98	10	8	8	44	42	43	0	−2	−3	151	154	155	164	167	169	53	51	51
NR	127	127	127	7	7	7	48	49	69	−1	−3	−3	226	229	237	250	259	262	102	107	105
IIR	25	19	18	1	2	3	9	9	8	0	−1	0	108	105	106	172	176	175	73	72	71
CR	98	99	97	23	21	20	58	56	60	0	−1	0	119	125	123	184	205	211	28	25	25
NBR	184	182	181	106	106	100	125	124	123	9	10	8	95	95	93	146	139	140	4	6	8
Weight Change, Percent																					
Ameripol CB	132	127	112	4	4	4	25	22	23	−2	−3	−3	148	138	148	204	206	205	41	41	40
SBR	106	105	98	5	4	3	27	26	27	0	−2	−3	109	112	112	151	155	156	30	29	29
NR	132	135	131	4	4	3	32	32	46	−1	−3	−3	169	169	176	233	243	246	63	66	64
IIR	28	23	21	0	2	1	6	5	5	0	−1	0	79	78	78	163	167	166	45	44	43
CR	88	89	83	11	11	9	31	31	32	0	−2	0	74	76	76	144	161	165	14	12	12
NBR	184	183	177	68	68	64	81	82	82	5	6	4	67	67	67	130	125	126	2	3	4

Solvent	N-Hexane			Nitropropane			Ethyl Acetate			Turpentine			Cottonseed oil			Mineral oil		
Days at Room Temperature	1	3	7	1	3	7	1	3	7	1	3	7	1	3	7	1	3	7
Volume Change, Percent																		
Ameripol CB	76	79	78	17	15	16	42	41	42	146	151	134	21	38	47	18	30	43
SBR	56	54	55	23	20	20	50	48	47	113	116	113	6	9	17	2	3	6
NR	124	133	134	13	12	13	46	48	51	183	201	209	14	27	50	12	21	37
IIR	166	166	168	0	0	1	11	9	7	237	265	247	1	0	0	5	9	15
CR	19	14	14	39	38	39	64	63	63	40	56	56	1	1	3	−1	−1	−1
NBR	1	2	3	147	150	151	80	81	80	0	2	3	0	0	1	0	−1	−1
Weight Change, Percent																		
Ameripol CB	43	44	44	15	13	14	32	32	33	106	108	96	16	29	36	14	23	32
SBR	29	28	28	19	17	17	37	35	35	80	81	78	4	7	13	17	3	4
NR	70	76	76	12	11	11	35	37	39	132	144	148	11	20	38	9	16	27
IIR	94	95	96	4	1	1	9	7	5	173	192	178	1	0	1	4	7	11
CR	8	6	5	28	27	27	40	40	40	24	33	33	1	0	2	0	0	−1
NBR	1	1	2	119	122	122	58	59	58	0	1	2	0	0	0	0	0	−1