The commercial development of pinic acid at low unit cost from α-pinene is eminently desirable as it is potentially available in large supply from turpentine, a native raw material. In addition to its use in synthetic lubricants, this dibasic acid has excellent possibilities for the synthesis of low temperature plasticizers, polymers, resins, and fibers.

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Extrusion Plasticity of a Butadiene-Acrylonitrile Rubber

EFFECT OF AMIDE-TYPE COMPOUNDS

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THE development of butadiene-acrylonitrile rubbers for uses involving high resistance to petroleum products quickly made evident the need of auxiliary agents, for example, plasticizers. It was first observed that the esters of *N*,*N*-dialkyldithiocarbamic acids were extremely effective as plasticizers for natural rubber. With this evidence as a lead, the dithiocarbamates, carbamates, amides, and imides, and the related oxazolines were investigated.

TESTING PROCEDURE

A butadiene-acrylonitrile polymer made by the B. F. Goodrich Chemical Co., known as Hycar OR-15, was selected for the basic material. The recipe used is shown in Table I (*13*).

The material was press cured 10, 20, 30, 45, and 60 minutes at 310° F. Curing was done according to ASTM D 15–41 and tension testing followed ASTM D 142–41. Except as noted in Table V the ratio of plasticizer to rubber was kept constant. The mixing technique was that specified by the manufacturer of the rubber (*14*).

Mechanical plasticizing was obtained by breaking down the rubber by repeated passes through the mill, holding the sheet formed out from the rolls, and then dropping it into the pan where it was massed and returned to the rolls. Several such passes through a very tight mill were made before the rolls were opened and a thicker continuous sheet was allowed to form. From this point the mixing procedure was, first, addition of the solids, and finally addition of the plasticizer, with adequate cutting and rolling to ensure dispersion.

Physical tests such as tensile strength and elongation were determined at room temperature (82° F.) using a Scott tensile

TABLE I. RECIPE (PARTS PER 100 PARTS RUBBER)

Hycar OR-15	100.0
Zinc oxide	5.0
Stearic acid	1.0
Sulfur	1.5
Benzothiazyl disulfide	1.5
Pelleted EPC carbon black	50.0
Plasticizer	30.0
	189.0

machine. The tests reported herein were run on the stock cured at 30 minutes. Plasticities were determined on the uncured stock by measuring the extrusion time at a 7.5-pound-per-square-inch ram pressure, using a Firestone Plastometer (*10*).

As an indication of the purity and identity of the plasticizer compounds tested, the boiling ranges and nitrogen analyses are given in the tables. In general, the Kjeldahl method was used for nitrogen analyses, but when this failed the Dumas method was employed.

A large number of the plasticizers which were prepared for the test work are new compounds. All those shown in the tables without a literature reference are new and characterized here for the first time.

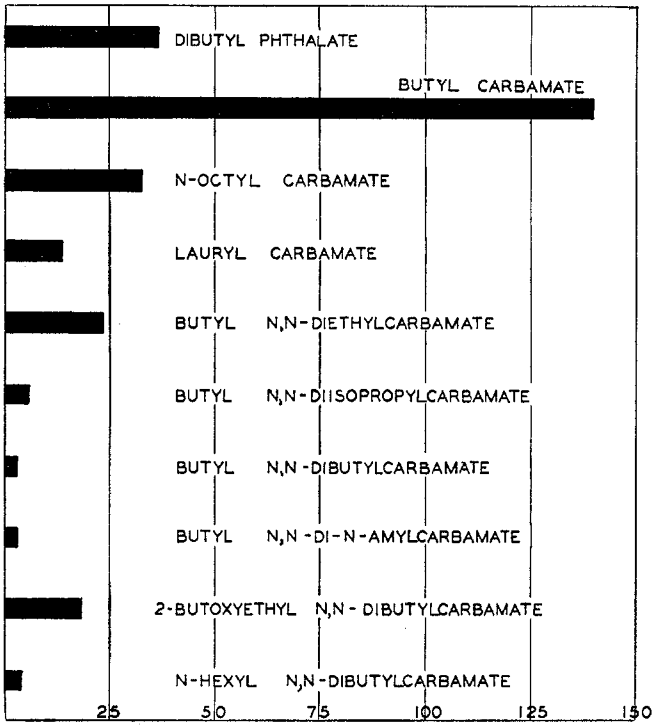
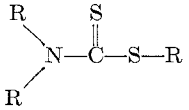


Figure 1. Effect of Carbamate Ester Structure on Extrusion Time

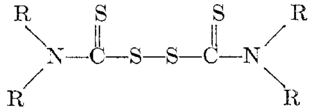
ALKYL *N,N*-DIALKYLDITHIOCARBAMATES

The use of dithiocarbamic acid derivatives in rubber is not new, but the use of esters of dialkyldithiocarbamic acids as plasticizers for a butadiene-acrylonitrile rubber is new. The method of preparation used was a modification of an old method wherein an aqueous solution of the sodium *N,N*-dialkyldithiocarbamate is treated with an alkyl halide (*5*).

The alkyl *N,N*-dialkyldithiocarbamates were first tested as accelerators in natural rubber. The 10% masterbatch was so plastic that it flowed overnight into a mass resembling a pool of liquid. The odor was somewhat offensive so attention was directed later to the oxygen analogs, which were reasonably free of this objection. The *N,N*-dialkyldithiocarbamate esters resemble the thiuramdisulfides in structure and therefore might be expected to have accelerating power.



Ester



Disulfide

To check this point tests were run in Hycar OR-15, as shown in Table II.

TABLE II. DITHIOCARBAMATE ESTERS AS ACCELERATORS[a] IN ACRYLONITRILE RUBBER

Cure at 310° F., Min.	Load at 400% Elong., Lb./Sq. In.		Tensile at Break, Lb./Sq. In.		Elongation at Break, %	
	A	B	A	B	A	B
15	500	490	580	580	490	563
20	1150	1150	1240	1270	440	500
30	1510	1650	1600	1710	417	410
45	2250	2200	2250	2300	400	410
60	2500	2720	2500	2720	400	400

[a] Recipes for accelerators A and B each include 100 parts Hycar OR-15, 5 parts zinc oxide, 1.5 parts sulfur, 1.0 part stearic acid, and 100 parts carbon black (FT). A contained 0 part butyl *N,N*-dimethyldithiocarbamate and B contained 1.0 part.

Both of the Hycar OR-15 stocks in Table II showed signs of vulcanization. The difference between A and B stocks was so slight that it is obvious that the ester, butyl *N,N*-dimethyldithiocarbamate, is not an accelerator under these conditions. While only the one ester was tested, the negative results were so emphatic that no other members of the homologous series were tested.

Table III presents the data on the homologous series of esters as plasticizers in the Hycar OR-15 stock.

All the compounds tested were plasticizers. Even the solid 1,2-ethane bis(*N,N*-dimethyldithiocarbamate) gave an extrusion time that was markedly less than the unplasticized control, the

TABLE III. PLASTICIZING EFFECTIVENESS OF ALKYL *N,N*-DIALKYLDITHIOCARBAMATES

Plasticizer	Boiling Range		Nitrogen, %		Performance in Hycar OR-15 Stock[a]		
	° C.	Mm.	Calcd.	Found	Tensile[b], lb./sq. in.	Elongation[b], %	Extrusion, time[c], sec.
Controls							
Dibutyl phthalate	...	..	...	...	2980	480	37
Dicapryl phthalate	...	..	...	...	2710	463	32
Tricresyl phosphate	...	..	...	...	2540	395	60
Butyl *N,N*-dimethyldithiocarbamate	170–175	25	7.91	7.80	2710	360	5
Butyl *N,N*-diethyldithiocarbamate	Not distilled		6.83	7.51	2700	485	8
Butyl *N,N*-diisopropyldithiocarbamate	Not distilled		6.00	4.12	2680	570	4
Butyl *N,N*-dibutyldithiocarbamate	163	1	5.37	5.24	2480	473	19
Butyl *N,N*-di(1-methylheptyl)dithiocarbamate	Not distilled		3.75	3.88	2460	280	5
Amyl *N,N*-diamyldithiocarbamate	160–180	17	4.62	4.30	2130	413	6
1,2-Ethane bis(*N,N*-dimethyldithiocarbamate)	189	M.p.	10.44	10.83	3370	315	65

[a] Basic recipe given in Table I; cured 30 minutes at 310° F.
[b] Tests at 82° F. using Scott tensile machine.
[c] Uncured stock, Firestone Plastometer, 7.5-pound-per-square-inch ram pressure.

Table IV. Plasticizing Effectiveness of Substituted Carbamates

Plasticizer	Boiling Range, ° C.	Boiling Range, Mm.	Nitrogen, %, Calcd.	Nitrogen, %, Found	Performance in Hycar OR-15 Stock[a] Tensile[b], lb./sq. in.	Elongation[b], %	Extrusion time[c], sec.
Controls							
Dibutyl phthalate	...	...	...	...	2980	480	37
Dicapryl phthalate	...	...	...	...	2710	463	32
Tricresyl phosphate	...	...	...	...	2540	395	60
Butyl carbamate (*1*)	53–54	M.p.	11.96	11.41	3090	525	140
n-Octyl carbamate (*1*)	98–100	0.3	8.09	8.12	2750	275	33
Lauryl carbamate (*1*)	160–180	1	6.11	5.62	3100	223	13
Ethyl *N*-butylcarbamate (*1*)	87–89	7	...	...	1680	340	192
Ethyl *N*,*N*-dibutylcarbamate (*1*)	101–103	6	...	...	2050	390	55
Ethyl *N*-phenylcarbamate (*1*)	49–51	M.p.	...	...	2720	383	58
Ethyl *N*,*N*-dipheny carbamate (*1*)	71–72	M.p.	...	...	2290	433	78
Butyl *N*,*N*-diethy carbamate	55	30	8.09	7.83	2400	396	23
Butyl *N*,*N*-diisopropylcarbamate	Not distilled		6.97	6.72	2900	410	6
Butyl *N*-isopropyl-*N*-(2-nitroisobutyl)carbamate	118–121	3	11.72	11.72	2600	347	102
Butyl *N*,*N*-dibutylcarbamate	256	Atm.	6.12	6.32	2420	450	3
Butyl 4-morpholinecarboxylate (*15*)	149–156	30	8.18	7.19	2170	380	18
Butyl 1-piperidinecarboxylate (*24*)	90–95	2	7.57	7.58	2650	455	43
Butyl *N*,*N*-di-*n*-amylcarbamate	Not distilled		5.34	6.21	2650	440	3
Butyl *N*,*N*-di(1-methylisopentyl)carbamate	288	Atm.	4.91	4.90	Incompatible	...	...
Butyl *N*,*N*-di(1-methylheptyl)carbamate	120–185	28	4.11	5.37	2840	447	5
Butyl *N*-isopropyl-*N*-tetrahydrofurfurylcarbamate	170–175	29	5.76	5.71	2040	380	9
Butyl *N*-[1-ethyl-4-(1-ethylpentyl)-3,5-dioxacyclohexyl]carbamate	215–225	27	4.27	4.24	3600	485	9
n-Amyl *N*,*N*-diisopropylcarbamate	234–235	Atm.	6.51	6.41	2260	417	8
n-Amyl *N*,*N*-dibutylcarbamate	271	Atm.	5.77	5.72	2900	397	4
n-Hexyl *N*,*N*-dibutylcarbamate	Not distilled		5.45	5.32	2730	430	4
Capryl *N*,*N*-diisopropylcarbamate	265	Atm.	5.44	5.49	2000	400	8
n-Octyl *N*-methylcarbamate	100–121	1	7.49	6.95	2040	250	29
n-Octyl *N*-phenylcarbamate (*1*)	120–165	1	5.62	5.53	2970	310	73
Lauryl *N*-methylcarbamate	140–175	1	5.76	5.40	2690	280	14
Lauryl *N*,*N*-dibutylcarbamate	166–171	0.3	4.12	3.90	Incompatible	...	...
Lauryl *N*-phenylcarbamate	155–200	1	4.59	3.76	2900	280	34
Benzyl *N*,*N*-dibutylcarbamate	81–82	1	5.32	6.31	2050	575	34
2-Nitroisobutyl *N*,*N*-dibutylcarbamate	134–135	0.3	10.21	10.71	1930	327	4
Diethylene glycol bis(*N*,*N*-dimethylcarbamate)	150–155	1	11.29	11.21	1890	217	30
Diethylene glycol bis(*N*,*N*-diisopropylcarbamate)	173–175	1	7.78	7.84	2700	480	30
Diethylene glycol bis(*N*,*N*-dibutylcarbamate)	200–208	1	6.73	6.77	1950	300	26
Diethylene glycol bis[*N*,*N*-di(1-methylisopentyl)carbamate]	Not distilled		5.30	5.31	Incompatible	...	...
2-Butoxyethyl *N*,*N*-dibutylcarbamate	145	1	4.84	4.85	2000	367	18
2-(Butoxyethoxy)ethyl *N*,*N*-dibutylcarbamate	147–152	1	4.41	4.48	2060	367	24

[a] Basic recipe given in Table I; cured 30 minutes at 310° F.
[b] Tests at 82° F. using Scott tensile machine.
[c] Uncured stock, Firestone Plastometer, 7.5-pound-per-square-inch ram pressure.

latter usually running 360 seconds. In these tests the nonaccelerating property is even more convincing, since 30 parts are added to a stock which already contains a vigorous accelerator. The authors did expect some activation of the primary accelerator, but there is no convincing indication of activation. Even slight traces of amine not removed during purification would activate the accelerator noticeably. This may have occurred in the case of butyl *N*,*N*-di(1-methylheptyl)dithiocarbamate. The elongation at break is low and the nitrogen analysis is somewhat higher than required by theory. Both of these facts suggest that some amine was activating the accelerator. For comparative purposes, stocks containing dibutyl phthalate, dicapryl phthalate, and tricresyl phosphate, respectively, are shown.

ALKYL *N*,*N*-DIALKYLCARBAMATES

The analogous oxygen compounds were synthesized by methods similar to those in the literature. This involved preparation of the chlorocarbonates by reaction of phosgene with an alcohol or phenol (*2*). The chlorocarbonates were then reacted with ammonia or an amine to give the carbamates (*6*). The results obtained in the base recipe with these plasticizers are listed in Table IV. When the stocks plasticized with the carbamates are compared with the esters used as controls, many of the carbamates were found to be even more effective plasticizers (*7*).

The effect of structure may be seen in two modes of variation in the alkyl groups. This is shown in Figure 1.

In the first case, the alkyl group on the ester portion of the carbamate was increased from butyl to *n*-octyl to lauryl. In this series the extrusion time changed from 140 to 33 to 13 seconds.

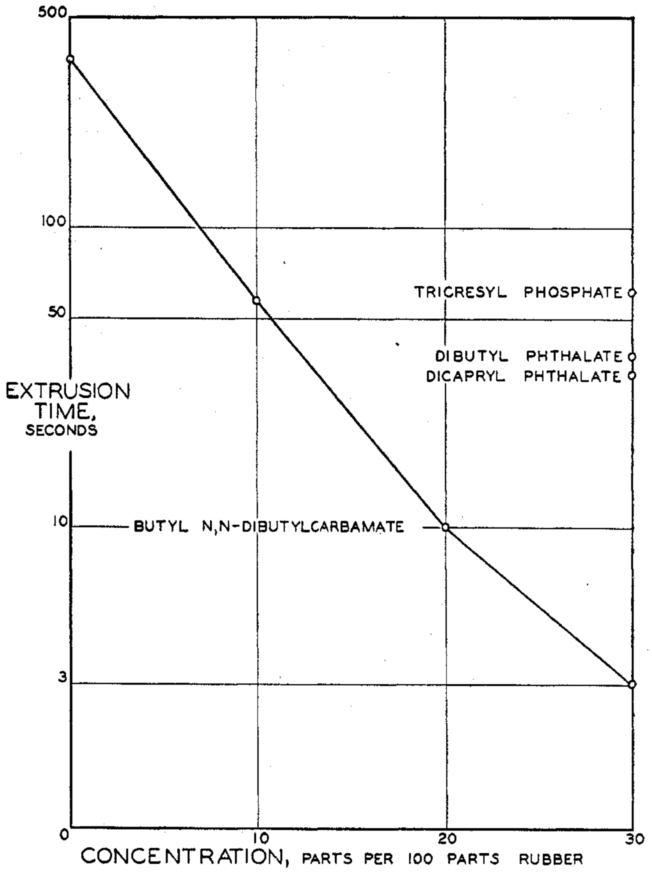


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Figure 2. Effect of Plasticizer Concentration on Extrusion Time

Table V. Plasticizing Effectiveness of Substituted Amides and Imides

Plasticizer	Boiling Range		Nitrogen, %		Performance in Hycar OR-15 Stock[a]		
	° C.	Mm.	Calcd.	Found	Tensile[b], lb./sq. in.	Elongation[b], %	Extrusion time[c], sec.
N,*N*-Dibutylformamide	98–108	7	8.92	8.98	2150	355	28
N,*N*-Diisopropylacetamide	196	Atm.	9.78	9.75	2100	330	57
N-Butylacetamide (*1*)	115–117	9	...	...	2300	297	13
N,*N*-Dibutylacetamide (*1*)	113–115	9	...	...	2530	357	7
N-Butyl-*N*-phenylacetamide (*1*)	143–146	15	...	...	2700	390	8
N,*N*-Di(1-methylisopentyl)acetamide	95–96	1	6.60	6.86	2250	700	30
N,*N*-Dibutylcaproamide	130	2	6.12	6.16	1460	340	5
N-Methylcapramide (*9*)	132–135	0.5	7.58	7.38	1860	310	0
N-Methyl-*N*-isopropylcapramide	113	0.1	6.17	6.11	1800	310	3
N,*N*-Dibutylcapramide	155–157	1	4.56	4.96	1460	355	10
N,*N*-Diisopropylpelargonamide	100–140	3	5.81	5.83	1580	293	13
N,*N*-Dibutylpelargonamide	170–175	4	5.16	5.34	2650	430	5
N,*N*-Diisopropyllauramide	172–178	0.6	4.94	4.81	1910	380	5
N,*N*-Dibutyllauramide	200–230	3	...	...	2520	450	4
N,*N*-Dibutylstearamide	227	2	3.54	3.71	Incompatible	...	...
N,*N*-Di-*n*-octylstearamide	258–262	0.3	2.67	3.03	Incompatible	...	...
N,*N*,*N'*,*N'*-Tetrabutyloxamide	150	0.1	9.27	9.31	2820	357	41
N-Methylsuccinimide (*1*)	100	0.1	12.37	12.33	1930	295	7
N,*N'*-Dimethylsuccinamide (*1*)	178	M.p.	19.42	19.19	Incompatible	...	...
N-Butylsuccinimide (*1*)	85–95	0.1	9.04	8.82	2280	340	4
N,*N'*-Dibutylsuccinamide	170	M.p.	12.28	11.71	1600	197	46
N-*n*-Octylsuccinimide	121–123	0.1	6.63	6.60	2450	546	8
N,*N'*-Di-*n*-octylsuccinamide	161–162	M.p.	8.24	8.35	1650	253	80
N,*N*,*N'*,*N'*-Tetrabutylsuccinamide	205–213	3	8.24	8.29	2410	243	28
N,*N*,*N'*,*N'*-Tetrabutyladipamide	Not distilled		7.60	7.61	2100	413	10
N,*N*,*N'*,*N'*-Tetraethylazelamide (*11*)	212–223	3	9.39	8.74	2990	353	208
N,*N*,*N'*,*N'*-Tetrabutylazelamide	233–234	2	6.83	6.83	2750	460	71
N,*N'*-Dimethylsebacamide (*3*)	239	0.5	12.25	11.75	2060	213	46
N,*N'*-Dimethyl-*N*,*N'*-diisopropylsebacamide	190–205	0.3	8.98	5.76	2580	353	100
N-Phenylsuccinimide (*1*)	149–151	M.p.	8.00	7.84	2360	257	78
N-(*o*-Nitrophenyl)succinimide (*1*)	155–157	M.p.	12.73	12.31	2870	390	209
N-(*m*-Nitrophenyl)succinimide (*1*)	161–162	M.p.	12.73	12.59	1920	300	347
N-(*p*-Nitrophenyl)succinimide (*1*)	210–211	M.p.	12.73	12.54	2520	237	126
N-(*o*-Chlorophenyl)succinimide (*16*)[d]	112	M.p.	6.67	6.46	2580	380	44
N-(*m*-Chlorophenyl)succinimide (*14*, *16*)	117	M.p.	6.67	6.58	2150	330	77
N-(*p*-Chlorophenyl)succinimide (*16*)	165	M.p.	6.67	6.54	2920	375	80
N-(2,4-Dichlorophenyl)succinimide	129–130	M.p.	5.74	5.67	2650	313	116
N-Butylphthalimide (*1*)	108–112	0.1	6.89	6.62	2710	415	13
N-*n*-Octylphthalimide (*1*)	140–144	0.1	5.40	...	2100	410	16
N-(*o*-Chlorophenyl)phthalimide (*17*)	134–135	M.p.	5.43	5.41	1750	503	154
N-(*m*-Chlorophenyl)phthalimide (*17*)	152–158	M.p.	5.43	5.40	3070	300	124
N-(*p*-Chlorophenyl)phthalimide (*1*)	183–187	M.p.	5.43	5.30	2850	347	220

[a] Basic recipe given in Table I; cured 30 minutes at 310° F.
[b] Tests at 82° F. using Scott tensile machine.
[c] Uncured stock, Firestone Plastometer, 7.5-pound-per-square-inch ram pressure.
[d] Melting points obtained do not agree with those reported by Sanna (*16*): *o*-isomer, m.p. 175° C.; *m*-isomer, m.p. 142° C. For the *m*-isomer, Haworth and Hey (*12*) report m.p. 119° to 120° C., in agreement with the value obtained in this work.

Similarly, the amide portion of the carbamate may be varied. The butyl *N*,*N*-diethyl-, *N*,*N*-diisopropyl-, *N*,*N*-dibutyl-, and *N*,*N*-di-*n*-amylcarbamates gave extrusion times of 23, 6, 3, and 3 seconds, respectively. This shows an increase in plasticizing power with the length of the alkyl group. However, it is possible to reach a combination of ester and amide alkyl groups that fails—for example, lauryl *N*,*N*-dibutylcarbamate was not compatible with Hycar OR-15.

In an effort to obtain higher boiling carbamates, various derivatives of ethylene glycol were used. The ether linkages existing in these compounds were not helpful. For example, 2-butoxyethyl *N*,*N*-dibutylcarbamate had an extrusion time of 18 seconds, while *n*-hexyl *N*,*N*-dibutylcarbamate had an extrusion time of 4 seconds. In general, the alkyl *N*,*N*-dialkylcarbamates are plasticizers for Hycar OR-15, but there are limits to the size of the alkyl group that may be placed on the ester or the amide portion of the molecule.

One of the most effective compounds was butyl *N*,*N*-dibutylcarbamate, but since the boiling point is 256° C., it was considered too volatile for many commercial applications. When tested at 10, 20, and 30 parts of plasticizer in 100 parts of rubber in the standard recipe, the data given in Figure 2 were obtained.

From this figure it appears that 30 parts of tricresyl phosphate are roughly equivalent to 10 parts of butyl *N*,*N*-dibutylcarbamate. Likewise, 30 parts of dibutyl phthalate approximate 11 parts of the carbamate, and 30 parts of dicapryl phthalate approximate 13 parts of the carbamate.

SUBSTITUTED AMIDES AND IMIDES

The preparation of the amides of monobasic acids followed standard methods—viz., either the reaction of an acid chloride or anhydride with the amine, the dehydration of the salt with benzene to remove the water azeotropically, or aminolysis of the ester.

The amides of dibasic acids were prepared from the corre-

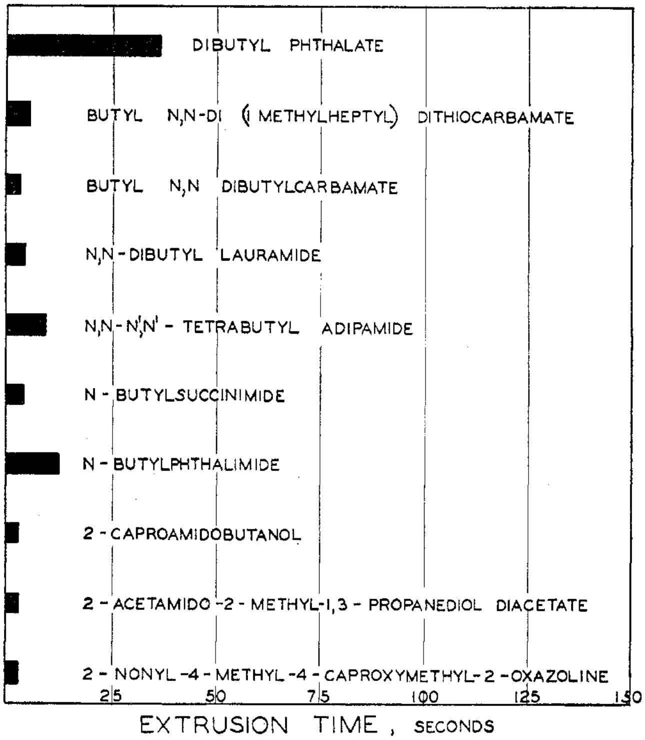

Figure 3. Types of Compounds

TABLE VI. PLASTICIZING EFFECTIVENESS OF ACYLATED AMINO HYDROXY COMPOUNDS

Plasticizer	Boiling Range		Nitrogen, %		Performance in Hycar OR-15 Stock[a]		
	° C.	Mm.	Calcd.	Found	Tensile[b], lb./sq. in.	Elongation[b], %	Extrusion time[c], sec.
2-Acetamidobutanol	Not distilled		10.7	9.7	2990	338	25
2-Caproamidobutanol	Not distilled		7.5	6.8	2240	365	3
2-Acetamido-2-methyl-1-propanol	Not distilled		10.7	9.3	3170	337	255
2-Acetamido-2-methyl-1,3-propanediol	Not distilled		9.5	8.5	3150	326	22
Tris(hydroxymethyl)acetamidomethane	Not distilled		8.6	8.2	2500	300	40
2-Acetamidobutyl acetate	138–140	3	8.1	8.1	3560	357	18
2-Acetamido-2-methyl-1,3-propanediol diacetate	Not distilled		6.1	6.1	3400	410	3
2-Phthalimidoisobutyl acetate	148–168	1–2	5.36	5.36	3110	390	28
2-Phthalimidoisobutyl laurate	212–220	1	3.49	3.74	3060	395	9
2-Phthalimido-2-methyl-1,3-propanediol diacetate	175–195	1	4.39	4.54	3860	440	41

[a] Basic recipe given in Table I; cured 30 minutes at 310° F.
[b] Tests at 82° F. using Scott tensile machine.
[c] Uncured stock, Firestone Plastometer, 7.5-pound-per-square-inch ram pressure.

TABLE VII. PLASTICIZING EFFECTIVENESS OF ESTERS OF HYDROXYMETHYLOXAZOLINES

Plasticizer, 2-R¹-4-R²-4-R³-2-oxazoline (*22*)			Boiling Range		Nitrogen, %		Performance in Hycar OR-15 Stock[a]		
R^1	R^2	R^3	° C.	Mm.	Calcd.	Found	Tensile[b], lb./sq. in.	Elongation[b], %	Extrusion time[c], sec.
Heptyl	Methyl	Capryloxymethyl	170–180	1–2	4.13	4.20	1840	440	9
Nonyl	Methyl	Caproxymethyl	200–210	1–2	3.54	3.54	2560	470	3
Undecyl	Methyl	Propionoxymethyl	170–190	2–3	4.30	4.30	2410	475	26
Phenyl	Methyl	Lauroxymethyl	235	1–2	3.75	3.70	2800	390	46
Phenyl	Methyl	Benzo-oxymethyl	195–214	2–3	4.75	4.71	3350	425	14
Ethyl	Ethyl	Propionoxymethyl	143	30	6.57	6.61	3100	550	4
Nonyl	Ethyl	Caproxymethyl	200–220	1–2	3.42	3.50	2170	395	4
Pentyl	Capro-oxymethyl	Capro-oxymethyl	170	2	3.52	3.58	2300	417	10
Heptyl	Capryloxymethyl	Capryloxymethyl	250–260	2	2.91	2.96	2000	365	7

[a] Basic recipe given in Table I; cured 30 minutes at 310° F.
[b] Tests at 82° F. using Scott tensile machine.
[c] Uncured stock, Firestone Plastometer, 7.5-pound-per-square-inch ram pressure.

sponding salts by heating well above the melting point and removing the water azeotropically with benzene. The dehydration generally proceeded with ease. The imides were prepared by reacting the amines with succinic acid or phthalic anhydride at elevated temperature, using benzene to remove the water of reaction by azeotropic distillation. The plasticizers prepared and the test results thereon are listed in Table V.

All of the monobasic acid amides presented in Table V which were compatible with Hycar OR-15 were effective plasticizers. The value of zero for *N*-methylcapramide indicates overplastization, a condition which can readily be corrected in practice. In general, the substituted amides did not bloom or sweat from either the uncured or cured stocks.

Of the dibasic acid amides tested (*8*), only *N,N,N′,N′*-tetraethylazelamide and *N,N′*-dimethyl-*N,N′*-diisopropylsebacamide were not effective, but this may have been due in part to impurities. The nitrogen analyses were not close to theory, which would indicate the existence in the materials of some of the monoamides. With succinic acid, only the alkylimides showed outstanding plasticizing action. In every case, the imide was superior to the corresponding diamide.

The arylimides of succinic and phthalic acids are of little value as plasticizers. The phenyl-, chlorophenyl-, and nitrophenylimides are far less effective than any of the alkylimides tested. All compounds of these classes gave extrusion times below the blank and can thus be called plasticizers, but they would be of no commercial use. *N*-Methylsuccinimide and *N*-butylsuccinimide are the most effective plasticizers in this group.

ACYLATED AMINO HYDROXY COMPOUNDS

For the present work, a series of acetamides was prepared from four of the amino hydroxy compounds derivable from the lower nitroparaffins by condensation with formaldehyde and subsequent reduction. One higher amide, 2-caproamidobutanol, was also prepared (*18*). In addition, two amide esters were prepared from these same amino hydroxy compounds by reaction with an excess of acetic anhydride (*21*). A series of imide esters was also prepared, starting with condensation of phthalic anhydride with the amino hydroxy compounds by a method similar to that of Wenker (*23*) and Billman (*4*). The resulting phthalimido alcohols were then esterified by conventional methods (*19*). The results on these compounds are listed in Table VI.

2-Caproamidobutanol is the outstanding plasticizer in this series. The hydroxyalkyl-substituted acetamides showed much higher extrusion times. Compared to 2-acetamidobutanol and 2-acetamido-2-methyl-1,3-propanediol, the corresponding acetates were more effective plasticizers (*21*). The phthalimidoalkyl esters also were effective, though not outstanding as a class (*19*).

ESTERS OF HYDROXYMETHYLOXAZOLINES

A series of esters of hydroxymethyloxazolines was prepared by condensation of polyhydroxy primary amines with organic acids (*22*). The data on stocks plasticized with these compounds are shown in Table VII.

When compared with the previous controls, dibutyl and dicapryl phthalates and tricresyl phosphate, all of the hydroxymethyloxazoline esters tested were effective plasticizers (*20*). The outstanding ones in the series are 2-nonyl-4-methyl-4-caproxymethyl-2-oxazoline and the corresponding 4-ethyl compound. These are shown in Figure 3 along with typical plasticizers from the other groups of compounds which gave low extrusion times.

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Houdriforming Reactions

STUDIES WITH PURE HYDROCARBONS

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HYDROCARBON reactions occurring in the Houdriforming of petroleum naphthas have previously been defined (*8, 11*) as dehydrogenation, dehydroisomerization, isomerization, hydrocracking, and dehydrocyclization. Houdriforming catalysts are polyfunctional, consisting of special preparations of precious metals of group VIII of the periodic table on an acid support. They possess primarily dehydrogenation and isomerization properties. (Referring to these two properties, the catalysts are also defined as dual function catalysts.) Under certain operating conditions the catalyst may promote some side reactions normally associated with cracking activity.

The use of complex hydrocarbon mixtures such as petroleum naphthas usually permits only group analyses and, while changes in composition and character of the naphthas can be followed, the ability of the catalyst to promote specific reactions is obscured. The present paper presents data obtained in the treatment of pure hydrocarbons and mixtures of pure hydrocarbons with a typical Houdriforming catalyst which throw some light on the type of reactions involved. Haensel and Donaldson (*5*) have recently described similar experiments for reforming with a different catalyst and at different conditions. The data presented here were obtained with hydrocarbons believed to be typical of those occurring in petroleum naphthas and at conditions which are similar to those used in naphtha reforming, not necessarily the optimum conditions for the specific reaction.

APPARATUS AND METHODS

Experimental equipment comprised an isothermal reactor consisting of a stainless steel tube in a lead bath. A stainless steel liner, 2.5 cm. inside diameter and 100 cm. long with a central axial thermocouple well, fitted snugly into the tube and contained the catalyst. The liner was welded to the reactor head and directly connected to the inlet lines to avoid channeling through the space between reactor and liner walls. Quick catalyst changes could be made by removing and replacing liner and reactor head with a second set.

The catalyst in the reactor, which in these experiments was a typical Houdriforming catalyst, was spaced with about an equal volume of quartz chips to prevent excessive temperature drops caused by endothermic reactions. Temperature gradients between lead bath and center of the catalyst bed were not more than ±3° F. The catalyst section was preceded by a quartz preheater section. Oil and hydrogen feed entered this section and were mixed in it after having passed separate coil preheaters in a lead bath. Hydrocarbons were charged with a Hills-McCanna pump and hydrogen was introduced from a high pressure cylinder through a high pressure rotameter. An automatic pressure controller (Gismo, Fisher Governor Co.) maintained constant pressure, either 300 or 600 pounds per square inch gage.

Reaction products were condensed in a coil condenser at operating pressure and liquid products were collected in one of two high pressure separators. The product stream was periodically switched between the separators, one of which was then depressurized prior to withdrawing liquid. Gas from the separators was depressurized in the pressure controller and metered in a wet-test gas meter, and samples were collected for analysis in a Consolidated Engineering Co. mass spectrometer.

Liquid product from the separators was stabilized to C_{5+} naphtha in a Podbielniak Heligrid column, 22-mm. inside diameter and 30 cm. long, at a 10 to 1 reflux ratio to a 75° F. overhead temperature. The stabilized product was separated into aromatic, olefinic, and paraffinic-naphthenic fractions by chromatographic adsorption and subsequent desorption on silica gel, following the principle of ASTM method D 936-49T. Both fractions were distilled in high temperature Podbielniak columns, 13-mm. inside diameter and 45 cm. long, at a 50 to 1 reflux ratio and a 50-plate efficiency. Individual cuts were analyzed by physical properties such as refractive index, infrared spectra obtained with a Perkins-Elmer spectrograph, etc. Amounts of individual compounds in the product were then converted to a charge basis and conversions were calculated under proper consideration of density changes. Weight balances were above 95 weight % and losses were distributed over products to obtain results on a no-loss basis.

Hydrocarbons used were obtained from Phillips Petroleum Co. in technical or pure grades and hydrogen (99.7%+) was procured from Liquid Carbonic, Inc.

EXPERIMENTAL RESULTS AND DISCUSSION

DEHYDROGENATION. The dehydrogenation of naphthenes to aromatics is of prime importance in Houdriforming, permitting production of a great number of aromatics from the corresponding cyclohexanes, of which benzene, toluene, and xylene are of most immediate commercial interest. Isomerization of cyclohexanes to methylcyclopentanes is undesirable for the production of aromatics because of the greater difficulty of converting methylcyclopentane to benzene, although the reverse reaction is, of course, desired and will be described later. The thermodynamic equilibrium is in favor of the alkylcyclopentanes over cyclohexanes at all temperatures under consideration.

Cyclohexane and methylcyclohexane were used as typical hydrocarbons in this study. Cyclohexane is dehydrogenated over the dual function catalyst to benzene in yields which are close enough to equilibrium even at a liquid hourly space rate of 3 to be considered equilibrium yields in view of the uncertainty of calculated equilibrium values (Table I). In all cases thermodynamic calculations have been made on the basis of data from API Project 44. At higher temperatures, such as 950° F., some cracking and isomerization of cracked products occur. Table II shows that a conversion of 99.7% is obtained at 950° F., 300 pounds per square inch gage, a liquid space velocity of 3 volumes per volume per hour and hydrogen to cyclohexane feed