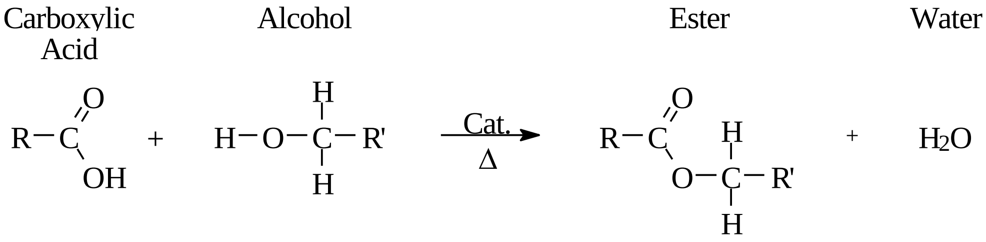
Ester Plasticizers for Polar Elastomers with Emphasis on Low-Temperature

Ester plasticizers contribute processing advantages to rubber compounds made with polar elastomers, much the same as petroleum oils do for low polarity rubbers. By definition, a plasticizer is *"a compounding material used to enhance the deformability of a polymeric compound."* The important contribution of esters, however, is the adjustment of rubber compound properties relative to fluid service. Fluid service, depending upon the particular application, may involve extraction resistance by fluids, resistance to volatilization, flexibility, low-temperature, compression set, resilience, and on and on. Attempts to describe the needs of applications have resulted in standardized bench tests that provide guidelines for compounds with satisfactory service characteristics.

Selection of ester plasticizers can be a very troublesome task. Hundreds of ester plasticizers are available, some are identified generically, but many only by tradename. Plasticizer manufacturers provide you with a list of properties that describe the esters. But what can you learn about the plasticizer from that data? Most monomeric plasticizers can be identified generically, but that information is not available for polymerics. Selection of esters that provide satisfactory service characteristics results from knowledge of both their (the plasticizers) contribution to compound properties and their chemical-physical properties.

Derivation

Raw materials, sources, esterification reaction examples etc., have been described recently by Kuceski(1) and Whittington(2). Briefly, the least complicated equation to describe the esterification reaction is for formation of a monoester.



Butyl oleate is an example of a monoester. Mono, di and tri-basic organic acids may be reacted with alcohols, glycols and polyols to form a great variety of esters. There also are other possible raw materials and mechanisms.

Monomeric Plasticizers

Testing by our Rubber and Plastics applications laboratory places much significance upon plasticizer permanence. Permanence is generally judged by changes in weight, volume, stress or strain measurements after test specimens have been exposed to standard aging conditions, In addition, our laboratory frequently tests low-temperature brittleness of test specimens that have been exposed to standard aging conditions. This provides a different kind of information than which you are normally accustomed. From a recent study with 34% [-C≡N] content NBR, of eleven monomerics tested, six have been selected for discussion. **TABLE I** shows compound low-temperature data and information relative to plasticizer structure. Such information may assist in plasticizer selection.

DOP is commonly tested as a control and it is also lower cost relative to other esters. DOA, another common ester, has experienced significant use in the past because of its contribution to as-molded, low-temperature. Neither DOP nor DOA exhibit good permanence after accelerated aging conditions at 125°C in air oven or oil immersion environments.

TABLE I

LOW-TEMPERATURE BRITTLENESS (ASTM D2137), °C
For NBR compounds containing MONOMERIC PLASTICIZERS tested after exposures shown. Compound: 34% [-C≡N] NBR, 20 pphr plasticizer (10.2% of compound).

			PLASTHALL			
Monomerics:	**DOP**	**DOA**	**DBEA**	**DBEEA**	**83SS**	**4141**
As Molded	-33	-42	-43	-40	-39	-42
After Air Oven, 70h/125°C	-25	-23	-27	-31	-34	-30
After ASTM 1, 70h/125°C	-26	-24	-25	-26	-25	-25
After ASTM 3, 70h/125°C	-24	-24	-25	-26	-23	-27
After Water, 70h/100°C	-34	-35	-37	-36	-35	-37
After Fuel C/Dry Out	-26	-22	-27	-27	-25	-25
Avg. Molec. Weight	391	373	346	494	505	430
Carbon/Oxygen ratio	6/1	5.5/1	3/1	2.75/1	3.5/1	4/1
.Structure*	BAB	BAB	EAE	EAE	EAE	AGA
Sap. Value	-	301	328	232	222	260

*A=Acid, B=Alcohol, G=Glycol, E--Ether Alcohol
Ref. (3)

Another structural feature of plasticizers that influences compound low-temperature is branching versus linear end groups. Diesters with linear end groups provide better low-temperature than is obtained from branched end groups when both contain an equal number of carbon atoms. The dioctyl groups of the above esters are branched

(2-ethylhexyl), while end groups of the other four are linear. It should be mentioned that while the data shown here is for only six of the eleven plasticizers tested, data from the remaining five agree with these findings.
Summarizing the data from ***TABLE I****:*

1. Best low-temperature after air oven aging occurred with the highest molecular weight monomeric plasticizers, those were ether or glycol diesters. The fourth best was with the lowest molecular weight of the six diesters, but it also is an ether diester. These four have the lowest carbon/oxygen ratios: 4/1 and less.

2. Low-temperature after water immersion shows that the compound with DOP experiences the least change, but that compounds with ether or glycol diesters actually achieved better low-temperature values.

3. Saponification values do not offer assistance in selection of diesters for compounds made from 34% [-C≡N] NBR polymer.

Polymeric Plasticizers, 10 pphr

Compounds containing polymeric plasticizers do not have as good original molded low-temperature values as similar compounds containing monomeric plasticizers. However, polymeric plasticizers, because they are less volatile during heat aging and less extractable during fluid (especially oil) aging than monomerics, may offer some advantage for after aged low-temperature values.

Several polymeric plasticizers were compared in 32% [-C≡N] NBR compounds and tested for nonbrittle low-temperature after aging. The test conditions were similar to those just discussed for monomeric plasticizers. Compounds for which data follows contained only 10 pphr plasticizer; data for 20 pphr will appear later. The plasticizer-characterization information is somewhat .different than appeared with monomeric plasticizers.

TABLE II

LOW-TEMPERATURE BRITTLENESS (ASTM D2137), °C for NBR compounds containing POLYMERIC PLASTICIZERS tested after exposures shown. Compound: 32 [-C≡N] NBR, 10 pphr plasticizer (5.4% of compound)

	PLASTHALL					
POLYMERICS:	**P-530**	**P-630**	**P-640**	**P-7035**	**P-7092**	**P-644**
As Molded	-27	-30	-28	-26	-25	-27
After Air Oven, 70h/125°C	-20	-19	-27	-22	-19	-21
After ASTM 1, 70h/135°C	-24	-18	-22	-24	-18	-24
After ASTM 3, 70h/135°C	-20	-24	-24	-23	-24	-27
After Water, 70h/100°C	-23	-15	-20	-25	-19	-27
After Fuel C/Dry Out	-10	-15	-17	-14	-20	-21
App. Viscosity at 25°C, cps	2.2K	2.6K	6.8K	11K	24K	110K
Av. Molec. Weight	2300	2200	3400	4500	5000	5000
Sap. value	559	530	535	498	520	555
Acid Type*	G	A	A	G	G	A

*G = Glutarate, A = Adipate

The range of losses of low-temperature after ASTM 1 and 3 Oil immersions compared to values for as-molded test specimens is from 0 to 12°C. The range of losses for the previously discussed group of monomeric plasticizers, from as-molded to after-oil immersion specimens, was 14°C to 18°C if the values for DOP are ignored. The original low-temperature value for DOP compound is considerably poorer than for the other diesters, and thus, its differentials were only 7°C to 9°C from as-molded to after-oil immersion values.

There are no clear conditions of good low-temperature after aging for these compounds containing 10 pphr polymeric as there were with the 20 pphr monomeric, except with P-644. The one characterizing plasticizer property that may help explain these low losses is viscosity.

Polymeric Plasticizer, 20 pphr

The data of **TABLE III** is for compounds with three polymerics at 20 pphr: P-550, G-30 and P-644, and one-monomeric at 20 pphr. There are some significant differences in plasticizer characterization property values that did not appear in the group of polymerics tested at 10 pphr. Saponification values of P-550 and G-30 are lower, showing lower polarity and the viscosity and molecular weight of G-30 are significantly lower.

What might be their influences? The actual low-temperature values of the G-30 compound are not good, some of the mixed acid constituency appear to be poor contributors to compound low temperature. However, the compound with G-30 shows low losses after aging. Saponification values appear not to offer assistance to plasticizer selection for compounds of medium-high [-C≡N] polymer.

The compound with P-644 shows 3°C improvement in low-temperature for its as-molded compound value. Its low-temperature after oil aging again appears good, as it did for compound with 10 pphr.

> *One curious item in all tests so far is low-temperature after water aging: Either the esters are not extracted to any significance; or water is absorbed and ice crystals are formed within the compound and they lubricate the polymer molecules; or glycol units break off the polyester and function as low-temperature plasticizers.*

TABLE III

LOW TEMPERATURE BRITTLENESS (ASTM D2137) °C
For NBR compound containing 20 pphr plasticizer
(10.2% of compound)

Plasticizer	Plasthall 4141	Plasthall P-550	Paraplex G-30	Plasthall P-644
Polymer NBR [-C≡N] content, %	**34**	**34**	**34**	**32**
As Molded	-41	-28	-25	-30
After Air Oven, 70h @ 125°C	-33	-27	-25	-25
70h/135°	-32	-27	-21	-
ASTM 1, 70h/125°C	-23	-21	-23	-
70h/135°C				-27
70h/149°C	-23	-21	-23	-
ASTM 3, 70h/125°C	-27	-23	-21	-
70h/135°C	-	-	-	-27
70h/149°C	-25	-21	-21	-
After Water, 70h/100°C	-37	-30	-27	-28
After Fuel C/Dry Out	-26	-21	-21	-18
App. Viscosity at 25°C, cps	25	3.7K	1.4K	110K
Avg. Molecular Wt.	430	2500	800	5000
Saponification value	260	480	425	555
Acid Type*	-	G	M	A

*A - Adipate, G = Glutarate, M = Mixed

Monomeric - Polymeric Plasticizer Blends, 20 pphr,

The NBR compound data that precedes this was for polymer of medium-high acrylo content (32% and 34% [-C≡N]). The data of this section is for 20%, 34% and 38% [-C≡N]. The plasticizers for this study of blends are:

TABLE IV

Plasticizer Blend Study

Monomeric:	20	13	7	-
Polymeric:	-	7	13	20
Monomeric:	4141			
Polymeric.	P-550, G-30			

There were two instances of incompatibility evidenced by exudation from cured, unstressed sheets, but this also caused some interesting results. PLASTHALL 4141, at 20 pphr, exuded from unstressed test specimens at room temperature for compounds with 20% [-C≡N] polymer. But when used in combination with either P-550 or G-30, the 20% [-C≡N] NBR compounds exhibited excellent low-temperature and there were no signs of exudation. It appears the polymeric may have helped compatibilize the monomeric plasticizer.

The polymerics of this study PLASTHALL P-550 and PARAPLEX G-30 are of quite different characteristics. Past work has generally shown that compatibility and permanence of polymeric plasticizers in NBR is relatable to polarity and viscosity. Saponification value, in spite of what we have found thus far, is considered a measure of polarity for polymeric plasticizers The higher the sap value, the more polar the polymeric plasticizer. PARAPLEX G-30 was expected to have a potentially greater compatibility problem than PLASTHALL P-550, because of its low viscosity and sap. value. It might not be compatible with highly polar NBR, 38% [-C≡N]. PLASTHALL P-550 has been shown to have excellent compatibility with PVC and with medium-high [-C≡N] HNBR. Its sap. value being higher than G-30 caused speculation that it would be compatible with 38% [-C≡N] NBR. P-550 was found to be incompatible at 20 pphr with the compound of 38% [-C≡N] and PLASTHALL 4141 did not compatibilize the polymeric that helped it with the low-acrylo NBR. PARAPLEX G-30 was compatible in the compounds of all three NBR polymers.

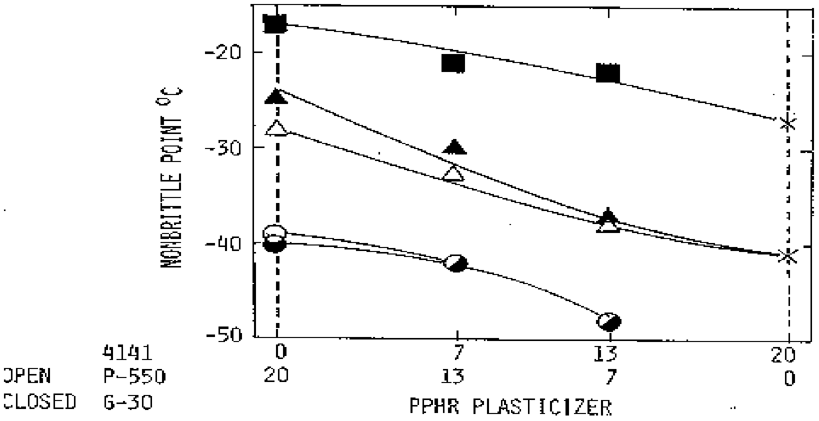
TABLE V

LOW-TEMPERATURE IMPACT (ASTM D2147), °C
For NBR compounds of 20%, 34%, 38% [-C≡N] polymers
Plasticizer at 20 pphr (10.2% Of compound)

	PLASTHALL				PARAPLEX		
Plasticizer	**4141**	**4141**	**P-550**	**P-550**	**G-30**	**G-30**	**G-30**
NBR, [-C≡N] %	**34**	**38**	**20**	**34**	**20**	**34**	**38**
As Molded	-41	-27	-39	-28	-40	-25	-17
After Air Oven, 70h/135°C	-32	-10	-35	-27	-37	-21	-10
After ASTM 1, 70h/149°22C	-23	-3	-30	-21	-33	-23	-5
After ASTM 3, 70h/149°C	-25	-10	-32	-21	-37	-21	-12
After Water, 70h/100°C	-37	-27	-38	-30	-42	-27	-16
After Fuel C/Dry Out (Ref. 4)	-26	-8	-33	-21	-35	-21	-4

TABLE V shows data for compounds of the plasticizers of this study, but unblended. These values serve as the "end-points" of this study of blended plasticizers. Figure 1 is a graph of the low-temperature nonbrittle point values for as-molded specimens only. The graph shows the change in nonbrittle point with changing blend ratio. It can be seen that low-temperature of blends is nearly directly proportional to the low-temperature of unblended components. The graph also shows the contribution of 4141 to the compound made with low [-C≡N] NBR.

FIGURE 1
LOW-TEMPERATURE (ASTM D2137)
CHANGE IN NONBRITTLE POINT OF NBR COMPOUNDS
WITH ○ 20% [-C≡N], △ 34% [-C≡N], □ 38% [-C≡N]



Trends from study of data for this polymeric-monomeric blend work revealed the following:

1. Low-temperature data for as-molded specimens of 34% and 38% [-C≡N]] was best for compounds plasticized with only monomeric plasticizer (PLASTHALL 4141).

2. Low-temperature values for compound of 38% [-C≡N], plasticized with blends of monomeric (PLASTHALL 4141) and polymeric (PLASTHALL P-550 or PARAPLEX G-30) plasticizers were equal or better after Air Oven ASTM 1 and 3 Oils and ASTM Fuel C immersions than any of the tested compounds containing only the polymeric or monomeric.
3. Low-temperature values for compounds of 20% [-C≡N], plasticized with blends of monomeric (PLASTHALL 4141) and polymeric (PLASTHALL P-550 and PARAPLEX G-30) plasticizers,

4. were equal or better after Air Oven, ASTM 1 and 3 Oils and Fuel C immersions than compounds plasticized only with the polymerics noted.

5. Low-temperature values for compounds of 34% [-C≡N], plasticized with blends of monomeric and polymeric plasticizers (identified in 2 and 3) were usually proportional to the plasticizer content of the blend, both for as-molded and after aged test specimens.

6. Relating compound low-temperature properties to characterization information of the plasticizer appears to be more difficult for polymeric plasticizers than monomerics. This may be the result of compatibility. The lowest saponification value polymeric showed the best compatibility with the range of [-C≡N] contents tested.

Plasticizer Characterization Data

Flash point and fire point tell you about the burning characteristics of the neat plasticizer. This may be important for storage locations and fire safety concerns. Freezing point is important for shipping and storage concerns, especially during winter months. Esters with high freezing points, e.g. above -30°F, may solidify during shipment or storage in your plant; they must be warmed until they become pourable or pumpable. Freeze point has little value for predicting low-temperature functionality in your compound.

Acid values are generally low and not of significant strength to affect cure retardation. Water content is not likely going to be a problem. Even when water is a by-product of the esterification reaction, the temperatures involved in the manufacturing process are far in excess of the boiling point of water. Thus, water is expelled from the reaction as steam.

Appearance and color are likely of interest only to people involved with other than black compounds. Dark or cloudy plasticizers, as opposed to light colored or clear plasticizers, are not necessarily signals of poor quality. Some of the more common plasticizers are dark in color. Epoxized soyabean oil forms crystals upon storage at 50°F or even prolonged storage at 70°0F, but that does not detract from its utility.

Saponification values measure the amount of carbonyl oxygen in the ester, it's a ratio of pendant oxygen to hydrocarbon content of the ester. It tells something about polarity of esters, but does not tell the complete story relative to compatibility. Viscosity plays a significant role relative to permanence, the highly viscous polymerics are generally more permanent than those of low viscosity.

Specific gravity is certainly of interest to you as it is related to your pound-volume cost.

Some of these data are of interest to you in plasticizer selection, but none of them unlocks the door to predicting plasticizer utility. Application testing is still the final selector. However, bench testing in representative recipes are useful in providing assistance for plasticizer selection.

SUMMARY

Data for low temperature impact testing has been discussed or several monomeric and polymeric esters in NBR of differing acrylonitrile [-C≡N] content. Comparison of nonbrittle point values obtained after subjecting test specimens to various aging conditions shows the possibility that low carbon to oxygen ratio for monomeric eaters combined with high molecular weight may be useful in selecting more permanent plasticizers. Polymeric plasticizers, if used in combination with monomeric plasticizers of limited compatibility, may assist in improving compound low-temperature. Plasticizer characterization data provides useful information about ester plasticizers, but provides little assistance relative to the effect in the compound. Prediction of the effects of plasticizers in compounds is still best obtained from bench testing in representative recipes.

REFERENCES

1. V.P. Kuceski, ***Plasticizers,*** unpublished work prepared for Rubber Division of ACS course, Intermediate Rubber Technology.
2. W.H. Whittington, ***Monomeric and Polymeric Ester (Polar) Plasticizers: A Review*****.** Presented at an Educational Symposium on Rubber Compounding, Spring 1983, Toronto, Ont., Canada, Rubber Division of American Chemical Society.
3. W.H. Whittington, ***Monomeric Plasticizers in NBR*****,** Report for Project 0172-112. The HallStar Company, 4-5-83.
4. W.H. Whittington and J. English, ***Plasticizer Blends with Varying Acrylo Content NBR***, Project 0249-112, Report currently not available, The HallStar Company.

RECIPE

(Polymer) - 100.00, Zinc Oxide - 5.0, Agerite Resin D - 1.0, Stearic Acid - 1.0, N-660 Black - 65.0,
(Plasticizer) - 10.0 and 20.0; Altax -2.0, Methyl Zimate - 1.5, Spider Sulfur- 0.4.
(Variables)

Mixing: Altax, Methyl Zimate and Sulfur were added on a two-roll laboratory mill to a master batch previously prepared in a BR Banbury. The masterbatch was prepared by a single pass mixing process. Vulcanization: Test slabs were prepared by curing them to an equal state-of-cure condition determined from an ODR curve.

TESTING

Testing was performed according to appropriate standards.

Low-Temperature Impact	ASTM D2137, A
Plasticizer Analysis	
Saponification Value	AOCS Cd 3a-63
Viscosity	ASTM D1824-72

RAW MATERIALS

Material	Description	Supplier
20% $[-C{\equiv}N]$, NBR	Chemigum N917	Goodyear Chemical
32% $[-C{\equiv}N]$, NBR	Hycar 1042	BFGoodrich Chemical
34% $[-C{\equiv}N]$, NBR	Krynac 34.50	Polysar, Ltd.
38% $[-C{\equiv}N]$, NBR	Paracril C	Uniroyal Chemical
Zinc Oxide	St. Joe 922	The HallStar Company
Agerite Resin D	Hydroquinoline antioxidant	R. T. Vanderbilt
Stearic Acid	Rubber Grade	The HallStar Company
N-660	Carbon Black	Cabot Corp.
Altax	Benzothiazyl disulfide	R. T. Vanderbilt
Methyl Zimate	Zinc dimethyldithiocarbamate	R. T. Vanderbilt
Spider Sulfur	Elemental Sulfur	The HallStar Company

PLASTICIZERS

All plasticizers reported here are available from The HallStar Company. All of The HallStar Company plasticizers listed below are accompanied by the tradename PLASTHALL®, except for G-30, its tradename is PARAPLEX®.

DOP	dioctyl phthalate (octyl-2-ethylhexyl)
DOA	dioctyl phthalate
DBEA	dibutoxyethyl adipate
DBEEA	dibutoxyethoxyethyl adipate
83SS	dibutoxyethoxyethyl sebacate substitute
4141	triethylene glycol caprate-caprylate
P-530	glutarate polyester, ≈2200 cps
P-630	adipate polyester, ≈2600 cps
P-640	adipate polyester, ≈6800 cps
P-7035	glutarate polyester, ≈11000 cps
P-7092	glutarate polyester, ≈24000 cps
P-644	adipate polyeoter, ≈110000 cps
P-550	glutarate polyetter, ≈3700 cps
G-30	mixed acid polyester, ≈1100 cps

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