# Evaluating Plasticizers for Elastomers Used in High-Temperature Applications

**Weight changes and low temperature flexibility after laboratory aging are used to determine the best plasticizers for acrylics and highly saturated nitriles.**

Acrylic and highly saturated nitrile elastomers are being used where application temperatures exceed the capabilities of traditional nitrile, polychloroprene and chlorosulfonated polyethylene (to 150°C). Many plasticizers commonly used with those traditional elastomers are too volatile, extractable or incompatible with the higher-performance elastomers. This article provides information about plasticizers that our research has shown are suitable for these high-performance acrylics and highly saturated nitriles.

Plasticizers are commonly used only for their as molded low-temperature contribution. Effective plasticizers for the above-named elastomers should have resistance to volatility and extraction at elevated temperatures. Weight changes and low-temperature flexibility after laboratory aging are indicators of plasticizer permanence. C.P. Hall uses both these properties extensively in our laboratory to identify and recommend suitable plasticizers.

There may be differences in performance from one polymer manufacturer's product to another. Testing polymers from all the producers is a gargantuan task; however, data for some of the similar materials from multiple producers are presented, including acrylics, such as Vamac B-124 MB and Hycar 4052, and highly saturated nitrites, such as Zetpol 2020, Tornac A, Tornac C and Therban 1707. See Table I for a comprehensive list of materials descriptions and sources used in this article.

Some people may believe plasticizers in this article are evaluated at unrealistically high levels. However, if the plasticizer does not detract significantly at those quantities, it will surely handle lower level needs effectively.

## Acrylic

**Vamac B-124 MB[1].** Plasticizers evaluated with Vamac B-124 MB were dioctyl sebacate (DOS), dibutoxyethoxyethoxyethyl adipate [DB(3E)A], dibutoxyethoxyethyl phthalate (DBEEP) and dialkyl diether glutarate (DADEG). Actually, two producers' DB(3E)As were tested, but only the data for C.P. Hall's material is represented here. Data for the two products are at least as similar as one would expect from two shipments by the same supplier. Testing for DBEEP was discontinued early; the material was experimental, and the numbers for compression set, low temperature and air-oven aging showed it lacked permanence.

## TABLE I
## Materials list

| Material | Description | Supplier |
|---|---|---|
| | | |
| Hycar 4052 | Acrylic ester copolymer | BFGoodrich |
| Vamac (B-124 MB) | Ethylene acrylic | DuPont Co. |
| Tornac A | Hydrogenated nitrile rubber | Polysar |
| Therban 1707 | Hydrogenated nitrile rubber | Bayer |
| Zetpol 2020 | Hydrogenated nitrile rubber | Nippon Zeon |
| Stearic acid | Stearic acid, rubber grade | Hallstar |
| TE-80 | Processing aid | Technical Processing |
| N-539 | Carbon black | Cabot Corp. |
| Magcarb L | Magnesium carbonate ($MgCO_3$) | Marine Magnesium |
| Na stearate | Sodium stearate | Hallstar |
| T(KD)D75 | 3-(3,4-dichlorophenyl)-11-dimethylurea, EPDM binder | Rhein-Chemie |
| Plasthall® P-670 | Polyester adipate(A1100) | Hallstar |
| Plasthall® 7050 | Dialkyl diether glutarate (DADEG) | Hallstar |
| Plasthall® 83SS | Dibutoxyethoxyethyl substitute sebacate(DBEESS) | Hallstar |
| RX-11806 | Dibutoxyethoxyethoxyethyl adipate (DB(3E)A) | Hallstar |
| TP-759® | Dibutoxyethoxyethoxyethyl adipate (DB(3E)A) | Morton International |
| Plasthall® P-7092 | Polyester glutarate(G24000) | Hallstar |
| Plasthall® P-7046 | Polyester glutarate(G11000) | Hallstar |
| Plasthall® P-7068 | Polyester phthalate(P800) | Hallstar |

## TABLE II
## Low temperature results for Vamac B-124MB

| Recipe variables | DOS | DB(3E)A | DADEG |
|---|---|---|---|
| | | | |
| **Brittleness** | | | |
| As molded | - 55 | -48 | -50 |
| After air oven (70 h at 149°C) | - 37 | -47 | -45 |
| | | | |
| **Torsion** | | | |
| **T-10,000,°C** | | | |
| As-molded | -48 | -45 | -42 |
| After air oven* | - | -45 | -40 |
| **T-45,000,°C** | | | |
| As-molded | - 56 | - 51 | -47 |
| After air oven* | -48 | -50 | -45 |
| **T-100,000, °C** | | | |
| As-molded | -62 | - 56 | - 51 |
| After air oven* | - 54 | - 56 | -49 |
| | | | |
| **Air Oven 70 h at 149°C** | | | |
| % Weight loss | -15 | -7.3 | -8.9 |

*7 days at 163°C

## TABLE III
## Fluid aging, % weight loss for Vamac B-124MB

| Recipe variables | DOS | DB(3E)A | DADEG |
|---|---|---|---|
| | | | |
| **ASTM No. 1 Oil, 70 h at 149°C** | -6.2 | -4.9 | - 0.24 |
| | | | |
| **ASTM No. 3 Oil, 70 h at 149°C** | +46 | +48 | +49 |
| | | | |
| **ATF (Dexron II-Texaco), 70 h at 149°C** | +8.1 | +8.9 | +9. 6 |

## TABLE IV
## Hycar 4052 recipe variables

| **N-539, PPHR** | 90.0 | 95.0 | 95.0 | 95.0 | 95.0 | 80.0 |
|---|---|---|---|---|---|---|
| | | | | | | |
| **$MgCO_3$** | - | 15.0 | 15.0 | 15.0 | 15.0 | - |
| | | | | | | |
| **Plasticizer** | | | | | | |
| **0 PPHR** | | **-** | **-** | **-** | **-** | **0** |
| **20 PPHR** | **DB(3E)A** | **DB(3E)A** | **A1100** | **DADEG** | **DBEESS** | **-** |
| | | | | | | |
| **Post-cure 4 h at 177 °C**<br>**% Weight loss** | 2.4 | 2.0 | 1.8 | 2.9 | 2.7 | 2.3 |

## TABLE V
## Low-temperature flexibility and air aging for Hycar 4052

| **Compound variables** | **0-$MgCO_3$ DB(3E)A** | **20-$MgCO_3$ DB(3E)A** | **A1100** | **DADEG** | **DBEESS** | **0-$MgCO_3$ 0-Plast** |
|---|---|---|---|---|---|---|
| | | | | | | |
| **Torsional stiffness** | | | | | | |
| $T_2$, °C | -36 | -34 | -30 | -30 | -31 | -20 |
| $T_5$, °C | -45 | -43 | -43 | -42 | -42 | -29 |
| $T_{10}$, °C | -49 | -48 | -47 | -47 | -47 | -32 |
| $T_{100}$, °C | - 56 | -56 | -56 | -54 | - 56 | -40 |
| | | | | | | |
| **Air oven 7 d at 177°C** | | | | | | |
| % Weight loss | 11.0 | 11.0 | 5.5 | 8.7 | 9.4 | 4.7 |

Low-temperature brittleness results (Table II) show the greatest change after heat aging is associated with DOS; changes with the other two materials are minor. While the DOS compound changes appear less severe for torsional stiffness testing than for brittleness, they are greater than the changes experienced with the other two plasticizers. Weight changes experienced after air-oven aging offer sufficient explanation for why the low-temperature differences occur. Thus, for Vamac B124 MB after heat aging, the most permanent plasticizer would be DB(3E)A, followed by DADEG and then DOS.

Permanence after fluid aging is also important, and it is believed low-temperature differences (whose data are not presented here) should be comparable with weight (and volume) changes that occurred with air aging (Table III). While permanence does not appear to show as much variation after fluid aging as after air aging, the order of most to least permanent appears to be DADEG, DB(3E)A and DOS.

**Hycar 4052.** This polymer, when plasticized, gave some molding difficulty, which was overcome by increasing compound hardness, adding magnesium carbonate or by becoming more familiar with handling. Magnesium carbonate was selected as an additive to reduce the molding difficulty experienced because a source indicated it could enhance mold flow and help eliminate entrapped air. Two plasticizers not tested with Vamac B-124 MB were added to this work. They were a low-viscosity adipate polymeric known to provide good low-temperature flexibility with other polymers (A1100) and a monomeric that offers reasonably good high- and low-temperature flexibility with nitrile rubber (DBEESS).

Because an oven post-cure of this material was necessary, weight loss was tested as a result of post-cure to determine if significant plasticizer loss results from that process. Variables of these recipes coupled with post-cure weight loss are shown in Table IV.

Interestingly, some of the plasticized compounds show less weight loss after oven post-cure than does the unplasticized control. However, the important finding is that the plasticized compounds showed no significantly different results from the unplasticized compound. Low-temperature flexibility after air aging was not tested for these compounds, but the results of these tests should be expected to follow the same pattern as occurred with the Vamac B-124 MB work.

These data show the compound with the low-viscosity polymeric experienced significantly less weight loss after heat aging than occurs with the other plasticizers. Coupling this with the unaged low-temperature flexibility and the knowledge of the Vamac B-124 MB shown earlier, the most to least permanent plasticizer order after heat aging is A1100, DADEG=DBEESS and DB(3E)A (Table V).

Less fluid testing was performed with the Hycar 4052, but the results are similar to those of the Vamac B-124 MB compounds (Table VI).

Low-temperature flexibility at low torsional twist force (T-2 and T-5) for plasticized compounds appears to favor the DB(3E)A plasticizer, but the others may be used without severe problems. All plasticizers tested provided better low-temperature flexibility than was obtained for the unplasticized control at all torsional twist forces. The extraction numbers are interesting in that the A1100 (polymeric) plasticizer showed least extraction by ASTM No. 1 oil and most swell by ASTM No. 3 oil. This type of result is similar to that found with nitriles. Another trend similar to that found for polymerics in nitrile compounds was the reduced swell range between ASTM No. 1 and ASTM No. 3 oils.

Plasticizers used with Hycar 4052 for low-temperature flexibility and permanence and heat and fluid aging resulted in the rearrangement of plasticizers from most to least effective as A1100, DB(3E)A, DADEG and DBEESS. The following conclusions are apparent from the testing of the two plasticized acrylic compounds.

- Plasticizers, when added to acrylic elastomer compounds, can reduce the low-temperature test values obtained compared to unplasticized compounds.
- Of the monomeric plasticizers tested, DB(3E)A and DADEG appear most effective. It should be noted these are the highest molecular weight of the monomeric esters tested.
- The low viscosity (and molecular weight) of polymeric A1100 appears to offer low-temperature flexibility and permanence suitable to acrylic elastomers.

It is my opinion that a large variety of ester plasticizers compatible with nitrile elastomers are also compatible with acrylics. However, because of the post-cure required by some acrylics and the higher maximum temperature of application, fewer plasticizers show a reasonable degree of utility with acrylic than with nitrile.

## Highly saturated nitrile

Acrylics, because of their polar character, can use a fairly large variety of ester plasticizers that also find use in nitrile rubber. Thus far, that does not appear to be the condition with highly saturated nitrites (HNBR). Possible causes of plasticizer compatibility problems with HNBR may be the polymer's lower degree of polarity due to lower unsaturation or its more crystalline character. The plasticizers used in nitrites that can also find use in HNBR are severely limited. Several questions arise.

- Can HNBR polymers benefit from plasticizers?
- If so, which plasticizers offer benefits and what benefits do they impart to the compounds (polymers)?
- Are the beneficial plasticizers useful to all HNBRS?

The degree or amount of unsaturation enters into the choice of recipe ingredients with these polymers, especially with cure systems. The most highly saturated (or least unsaturated) materials require peroxides to achieve effective states of cure. Does that have an impact on plasticizer choice? We believe so.

**TABLE VI**
**Weight change after fluid aging for Hycar 4052**

| **Recipe variables** | **N539/90 - DB(3E)A** | **N539/95 MgCO$_3$/15 DB(3E)A** | **→ A1100** | **→ DADEG** | **→ DBEESS** | **N539/80** |
|---|---|---|---|---|---|---|
| | | | | | | |
| **ASTM No. 1 Oil**, 70 h at 150°C | -7.0 | -5.3 | -1.4 | -4.5 | -5.1 | +.27 |
| | | | | | | |
| **ASTM No. 3 Oil**, 70 h at 150°C | + 5.1 | +6.9 | +9.5 | +8.3 | +7.9 | +13 |
| | | | | | | |
| **Σ % Weight changes** | 12.1 | 12.2 | 10.9 | 12.8 | 13.0 | 13.3 (13.0) |

## TABLE VII
## Plasticizer results with peroxide-cured HNBR

| **Plasticizer variables** | **None** | **8-10TM 20 PPHR** | **G24000 20 PPHR** |
|---|---|---|---|
| | | | |
| **As molded** | | | |
| **Duro A** | | | |
| Therban 1707 | 80 | 68 | 73 |
| Tornac A | 79 | 69 | 73 |
| Zetpol 2020 | 81 | 71 | 75 |
| **Gehman Torsion**, °C at 10,000 psi (flexibility) | | | |
| Therban 1707 | -28 | -37 | -29 |
| Tornac A | -27 | -35 | -27 |
| Zetpol 2020 | -27 | -37 | -31 |
| | | | |
| **Air Oven,** 7 d at 150°C, % weight change | | | |
| Therban 1707 | -2.3 | -2.5 | -2.4 |
| Tornac A | -2.4 | -2.6 | -2.4 |
| Zetpol 2020 | - 2.0 | -2.1 | -1.9 |
| | | | |
| **Low-Temperature Impact**, °C (brittleness) | | | |
| Therban 1707 | -46 | -53 | -46 |
| Tornac A | -38 | -53 | -38 |
| Zetpol 2020 | -45 | - 50 | -41 |

**HNBR-peroxide-cured.** Highly saturated HNBR may sound redundant, but the amount of unsaturation varies. The materials that must be peroxide-cured for maximum effectiveness probably are in the range of only one percent unsaturation. The acrylonitrile content still provides a high degree of oil resistance, but the amount of double bonds available is insufficient for effective sulfur vulcanization.

C.P. Hall has developed data for these recipe types that showed comparative data for Therban 1707, Tornac A and Zetpol 2020. Each polymer was plasticized with 20 PPHR first of a trimellitate and second of a polymeric[2]. The choice of these plasticizers was the result of testing a large variety of plasticizers, including several experimentals, most of which were either incompatible or offered nothing, after looking at the economics, that made them better than the first two.

Consider again the three questions. The answer for the first question using the data mentioned (Table VII) is yes for each of the three polymers. Regarding question two, if yes, which plasticizers should be used and how do the compounds benefit? The polymeric plasticizer for data presented can be identified by G24000. The monomeric trimellitate is identified by its generic character as 8-10TM. It is necessary to identify a particular trimellitate because all are not equal. The answer to the third question of whether beneficial plasticizers are useful to all HNBRs is possibly.

We have done more testing using Tornac A with commercial esters and can provide a list of additional materials that are satisfactory upon request.[3]

**TABLE VIII**
**Plasticizer results with sulfur HNBR**

| | G24000 | G11000 | P800 | Unplasticized |
|---|---|---|---|---|
| | | | | |
| **As Molded** | | | | |
| Low temperature brittleness, °C | -44 | -43 | -46 | -38 |
| Torsional stiffness, $T_{10}$, °c | -26 | -28 | -31 | -27 |
| | | | | |
| **After Air Oven,** 70 h at 150°C | | | | |
| Torsional stiffness, $T_{10}$, °C | -25 | -24 | - 23 | -19 |
| Weight change, % | -1.4 | -1.6 | -4.2 | -.94 |
| | | | | |
| **ASTM Fuel B,** 48 h at 40°C, dry out 24 h at 70°C | | | | |
| Torsional stiffness, $T_{10}$, °C | -30 | -29 | -30 | -27 |
| Weight change, % | -2.4 | -3.2 | -7.4 | -.02 |
| | | | | |
| **ASTM Fuel B (80) Ethanol (20**), 48 h at 40 °C, dry out 24 h at 70 °C | | | | |
| Torsional stiffness, $T_{10}$, °C | -30 | -29 | -29 | -30 |
| Weight change, % | -4.6 | -5.7 | -8.9 | -0.1 |
| | | | | |
| **Distilled Water,** 70 h at 100°C, dry out 24 h at 85°C | | | | |
| Torsional stiffness, $T_{10}$, °C | -29 | -28 | -30 | -26 |
| Weight change, % | -4.2 | -4.0 | -1.2 | -1.2 |

**Sulfur-cured HNBR.** A Zetpol 2020 sulfur-cured recipe with 20 PPHR plasticizer of G24000, G11000 and P800 polymerics was compared to an unplasticized recipe[4]. For all three elastomers, except Zetpol 2020, both 8-10TM and G24000 at 20 PPHR plasticizer provided better low-temperature brittleness than occurred with unplasticized compounds (Table VIII). Testing by torsional stiffness, all numbers were better for plasticized than unplasticized compounds. Other advantageous differences are:

- Lower compound Mooney viscosity at 150°C
- Longer time to five point rise with Mooney test
- Equal weight losses after 70 h at 150°C in air
- Shifted, but nearly equal, swell range numbers for ASTM Nos. 1 and 3 oils

Disadvantages include:

- Ever so slight increase in weight loss after the cycle of water immersion and drying for plasticized compounds
- Probable total extraction of 8-10 trimellitate by Fuel C, but one half or less extraction with the G24000 polymeric

The addition of plasticizers did not cause loss of low-temperature flexibility after aging and may have aided in better numbers after water aging. Work with Tornac C indicates similar aging should be expected and shows that six additional plasticizers are compatible.

**Conclusion**

Information has been presented for plasticizers that can be used with two elastomer types expected to service 150°C: acrylic and highly saturated nitrile. The plasticizers found effective with these are different for each of the two elastomer types. The data shows that compound weight loss is a reasonably good predictor of plasticizer permanence and retention of low temperature after aging.

**References**

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