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Technical Information

BULLETIN ORS-702

HERCOFLEX® 600, 707, 707A Plasticizers Comparison With Commercial Plasticizers in PVC Formulations

HERCOFLEX® 600, 707, and 707A plasticizers, which are fatty acid esters of pentaerythritol, function as high-performance plasticizers in polyvinyl chloride (PVC) and rubber formulations. The results in this bulletin compare the performance of Hercoflex plasticizers with competitive plasticizers used in the PVC industry. Data on plasticizer permanence, thermal oxidative stability, softening efficiency, and cold-temperature performance were obtained on PVC compositions containing the plasticizers shown in Table I.

Table I
Plasticizers Evaluated

Number and Designation ^(a)	Trademark	Generic Description	Supplier
1-H600	Hercoflex 600	Pentaerythritol ester	Hercules
2-H707	Hercoflex 707	Pentaerythritol ester	Hercules
3-H707A	Hercoflex 707A	Pentaerythritol ester	Hercules
4-DOP	Eastman DOP	Di-(2-ethyl hexyl)phthalate	Eastman
5-DINP	Jayflex DINP	Diisononyl phthalate	Exxon
6-TOTM	Kodaflex TOTM	Trioctyl trimellitate	Eastman
7-TIDTM	Nuoplas TIDTM	Triisodecyl trimellitate	Hüls
8-S148	Santicizer 148	Isodecyl diphenyl phosphate	Monsanto
9-S2148	Santicizer 2148	Alkyl aryl phosphate	Monsanto
10-PG54	Paraplex G54	Polyester adipate	C.P. Hall

^(a)Plasticizer number and designation (reference Figures 1 through 12) are assigned for ease of comparison.

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Results

All three Herculflex® plasticizers exhibit outstanding permanence comparable to the trimellitates and the polymeric PG54. The lower molecular weight (MW) H600 is more volatile than the higher MW H707 and H707A but far outperforms the phthalate and the phosphate plasticizers.

H600 and H707 have unusually good thermal oxidative stability as measured by high-pressure oxygen differential scanning calorimetry (DSC). Polymeric PG54 exhibits similar good stability. The phosphates give results that are not interpretable by this test.

Retention of tensile elongation after oven aging is best for the polymeric PG54, followed closely by all three Herculflex plasticizers and the trimellitates. The phthalates and phosphates performed very poorly in this test.

H600 shows excellent softening efficiency, much like the phthalates and phosphates. H707 and H707A are less efficient, similar to PG54 but better than TIDTM.

H600 has outstanding low-temperature performance, better than DOP. H707 and H707A have low-temperature performance similar to TIDTM but better than the polymeric PG54.

Conclusion

Herculflex plasticizers offer a unique combination of high permanence, oxidative stability, efficiency, and low-temperature performance. Other plasticizers may provide better performance in any one of these properties, but none can offer the balance of performance exhibited by Herculflex plasticizers. (See Table II.)

Table II
Summary of Plasticizer Performance in PVC

Property	Order of Performance					
	Best -----> Worst					
Permanence	PG54	H600	S2148	DINP	S148	S148
	TIDTM					
	TOTM					
	H707					
	H707A					
Thermal Oxidative Stability ^(b)	H600	PG54	H707	TOTM	DOP	H707A DINP TIDTM
Retention of Elongation ^(c)	PG54	H707	H600	S2148	DINP	S148 DOP
		TOTM				
		H707A				
		TIDTM				
Softening Efficiency	S2148	TOTM	H707A	H707	PG54	TIDTM
	S148					
	DINP					
	H600					
Low-Temperature Performance	S2148	H600	DOP	DINP	TIDTM	PG54
			S148	TOTM	H707	
					H707A	

^(b)High-pressure DSC.

^(c)Oven aging, 136°C.

Sample Preparation

Table III lists the weights of ingredients used to prepare the PVC formulations in this bulletin.

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Table III
Ingredients Used to Prepare PVC Formulations

<u>Ingredient</u>	<u>Supplier</u>	<u>Formulation, g</u>		
		<u>No. 1</u>	<u>No. 2</u>	<u>No. 3</u>
Geon 30 polyvinyl chloride resin	The Geon Company	98.3	89.1	81.5
Plasticizer ^(d)	(See Table II.)	44.3 (45 phr)	53.5 (60 phr)	61.1 (75 phr)
Paraplex G-62 epoxidized soybean oil	The C.P. Hall Company	5.0	5.0	5.0
Synpron 1976 stabilizer	Synthetic Products Company	2.5	2.5	2.5

^(d)Phr refers to the grams of plasticizer in the formulation for every 100 grams of PVC.

Fluxing of the PVC formulations was conducted on a steam-heated, two-roll mill. The front roll of the two-roll mill was operated at approximately 1.33 times the rpm of the back roll. Both rolls were heated to 340°F. The above blends were placed on the mill and allowed to preheat 2 min prior to starting the rolls turning. The blends were then fluxed on the two-roll mill for 2 min with a small gap setting. Following this, the gap was opened slightly to obtain a rolling band of PVC that was then cross-cut three times on each side over a period of 3.5 min. The gap was then opened once more, and after 1 min the compounds were removed from the two-roll mill and placed between two metal plates to cool. The total milling time from the start of rolling was 6.5 min.

The sample compounds, prepared on the two-roll mill, were then shaped under heat and pressure into uniform test sheets of the required thickness by using a heated hydraulic press. Picture frame molds were used along with ferrotype sheets on either side of the compound. Stacking several small, cut pieces of the thin-milled PVC in the center of the picture frame molds resulted in test specimens that were free of air bubbles. The molding cycle shown in Table IV was used to prepare test sheets for this study.

Table IV
Molding Schedule

<u>Temperature, °F</u>	<u>Time, min</u>	<u>Pressure, lbs</u>
Room to 340	8-10	0
340	15	17,500
340	3	20,000
340	3	37,500
100	8-10	37,500

Permanence and Migration of Plasticizers

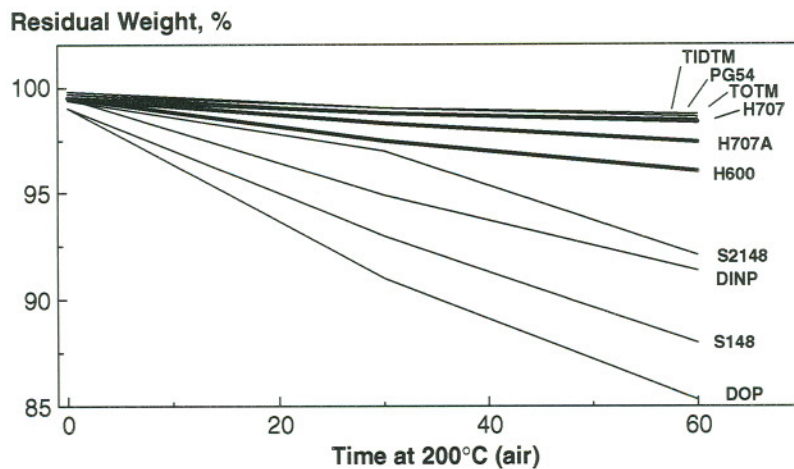
The properties of a compounded plastic like PVC change if the plasticizer migrates or evaporates from the PVC during use. Thus, permanence of the plasticizer in the PVC is needed for long-term performance. For high-temperature applications, such as wire and cable, plasticizers with a high degree of permanence must be used.

In this study, we examined permanence on molded PVC specimens containing 60 phr plasticizer (35.6% by weight plasticizer) by three separate methods:

1. Weight loss by thermal gravimetric analysis (TGA)
2. Volatile loss by ASTM D 1203
3. Weight loss in tensile bars during oven aging

TGA was run in air by heating to 200°C, holding for 1 hr, and monitoring the weight loss after 1 hr. Figure 1 shows the results graphically. Under these conditions, PVC formulations with H600, H707, H707A, TOTM, TIDTM, and PG54 retain greater than 95% of their original weight. Those with DINP and S2148 retain >90% of their original weight. DOP and S148 retain >85% of their original weight.

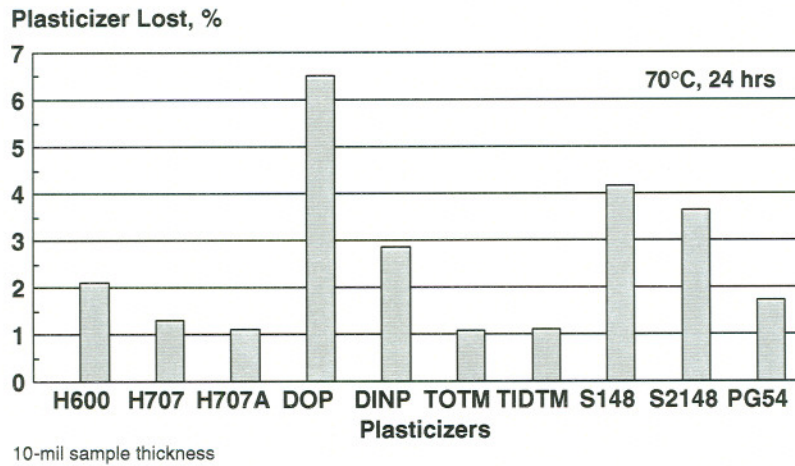
Figure 1
Weight Loss by TGA With 60 phr Plasticizer



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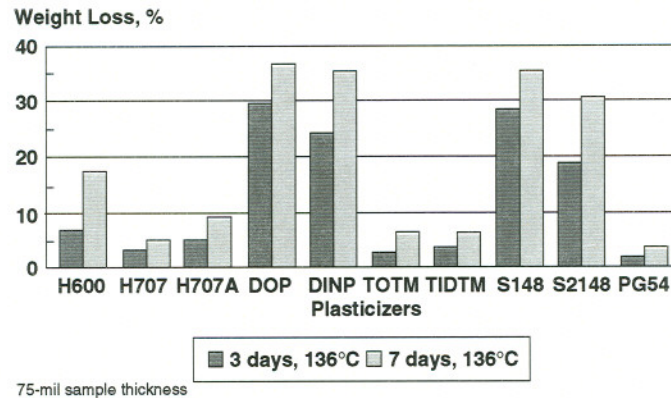
Volatile loss by ASTM D 1203, method A, involves direct contact between 2-in.-diameter, 10-mil-thick PVC samples and carbon black, heated at 70°C for 24 hrs. This test measures the loss of plasticizer by both migration and volatility and does not distinguish between the two mechanisms. The results are presented graphically in Figure 2. PVC samples with H600 lose 2.1% by weight of plasticizer. H707, H707A, the trimellitates, and the polymeric PG54 all lose less than 1.75% by weight of plasticizer. The phthalates and phosphates lose significantly higher levels of plasticizer.

Figure 2
Plasticizer Lost in PVC With 60 phr Plasticizer, %
Activated Carbon Method, ASTM D 1203



Molded PVC tensile specimens (75 mils thick) were oven aged at 136°C and tested at 3 and 7 days for retention of elongation. (See page 7, "Thermal Oxidative Stability".) The average weight loss of the samples was monitored and the results of the weight loss are shown in Figure 3. The results compare well with the previous two tests. PVC samples with DOP, DINP, S148, and S2148 all lose greater than 30% by weight after 7 days, H600 loses about 17%, and the remaining samples lose less than 10% by weight.

Figure 3
Weight Loss of PVC with 60 phr Plasticizer in Tensile Aging Test



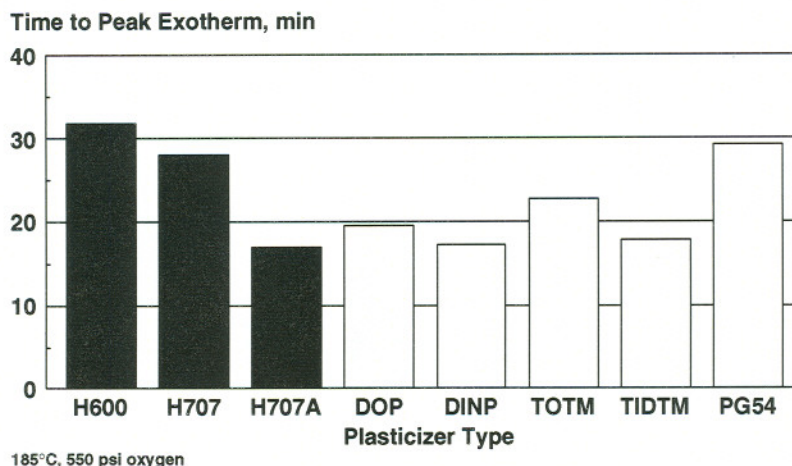
The polymeric PG54, the trimellitates, and the three Hercoflex® plasticizers (especially H707 and H707A) all have excellent permanence characteristics in PVC. In general, the order of permanence from best to worst is:

PG54~TOTM~TIDTM ~ H707 ~ H707A > H600 >> S2148>DINP> S148 ~ DOP

Thermal Oxidative Stability

High-pressure DSC (180°C, 550 psi oxygen) is an accelerated test that measures the relative oxidative stability of materials. The longer it takes a sample to exotherm, the more oxidatively stable the material is. In this study, where the only variable is the type of plasticizer in PVC (all at 60 phr), the results indicate the effect on oxidative stability due to the plasticizer alone. The results are shown graphically in Figure 4. The data for Santicizer 148 and 2148 were difficult to interpret (no definitive peak) and are omitted from the graph. Both H600 and H707 exhibit unusually good oxidative stability relative to the trimellitates and the phthalates.

Figure 4
High-Pressure DSC of PVC With 60 phr Plasticizer

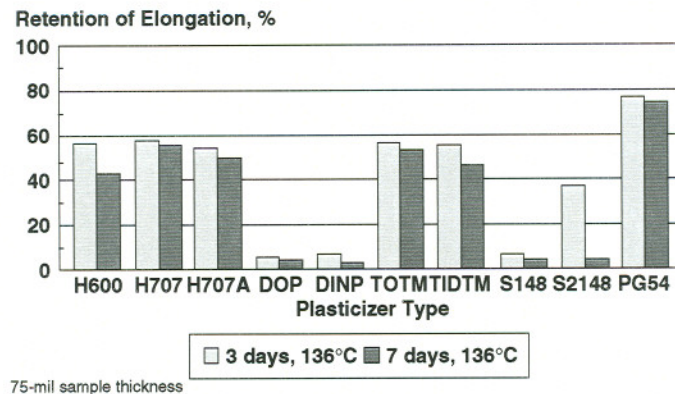


Most esters decompose with heat or light via a mechanism that involves β -hydrogens in the alcohol portion of the ester. The chemical structure of pentaerythritol (from which the Hercoflex[®] plasticizers are derived) contains no β -hydrogens and thus confers inherent thermal and light stability to the resulting ester. Similar esters made by Hercules Incorporated are used in jet engine lubricants that must withstand severe thermal oxidative conditions. The order of thermal oxidative stability, as measured by this test is:

H600 > PG54 > H707 >> TOTM > DOP > H707A~DINP~TIDTM

After oven aging, elongation of flexible PVC is reduced primarily due to loss of plasticizer, but oxidation during aging may also play a part. Retention of tensile elongation at break after aging is an important basis for the Underwriters Laboratories (UL) temperature ratings for wire and cable insulation and jacketing. The rating is based on the percentage of the original elongation retained after oven aging at a specified temperature for a specified length of time. For example, for a 90°C or 105°C UL rating, the samples must retain at least 65% of the original elongation after aging at 121° and 136°C, respectively. Figure 5 shows retention of elongation after oven aging at 136°C for 3 and 7 days for compounded PVC containing 60 phr of a series of plasticizers. This formulation was not optimized for wire and cable use and the results cannot be compared directly to the UL standards. The results indicate, however, that Hercoflex plasticizers compare well to trimellite plasticizers which are commonly used in wire and cable compounds. PG54 retains the most elongation after aging for 7 days (~75%). H707, TOTM, and H707A retain greater than 50% elongation. TIDTM and H600 retain greater than 40% elongation. The phthalates and phosphates have lost most of the plasticizer and retain little to no elongation after 7 days.

Figure 5
Retention of Elongation After Aging of PVC Compounds
With 60 phr Plasticizer



Softening Efficiency of Plasticizers

The softening efficiency of a plasticizer is important to manufacturers of PVC because it relates directly to the amount of plasticizer required to achieve a specific "hardness." There are numerous ways of measuring the softening efficiency of plasticizers. In this study, the softening efficiency was studied by three methods:

1. Tensile modulus at 100% elongation vs plasticizer level
2. Tensile modulus at 100% elongation vs Shore A hardness
3. Glass transition temperature by dynamic mechanical analysis (DMA) vs plasticizer type

Figures 6-8 show plots of the modulus at 100% elongation values for PVC compounds containing three levels of 10 different plasticizers. Figure 6 contains all the data together, and Figures 7 and 8 include the data from the more and less efficient plasticizers, respectively. The data suggest that the most efficient plasticizers are all quite similar (Figure 7) and that the less efficient plasticizers are also quite similar, with the exception of TIDTM, which is the least efficient of all of the plasticizers tested (Figure 8). If, for example, a PVC formulation with 1,100 psi tensile modulus at 100% elongation is required, 50-55 phr of the more efficient plasticizers (DOP, H600, S148, S2148, and DINP), 63-65 phr of the less efficient plasticizers (H707, H707A, TOTM, and PG54), and 72 phr of TIDTM would be required.

Figure 6
Tensile Modulus at 100% Elongation vs Plasticizer Level in Molded PVC

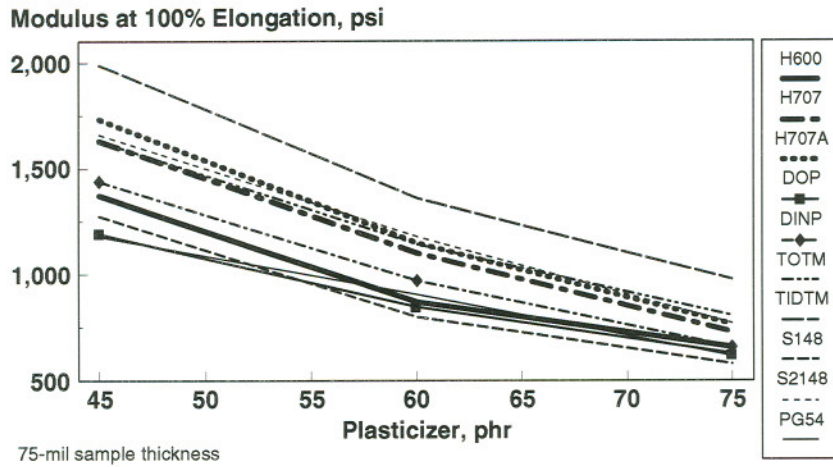


Figure 7
Tensile Modulus at 100% Elongation vs Plasticizer Level in Molded PVC

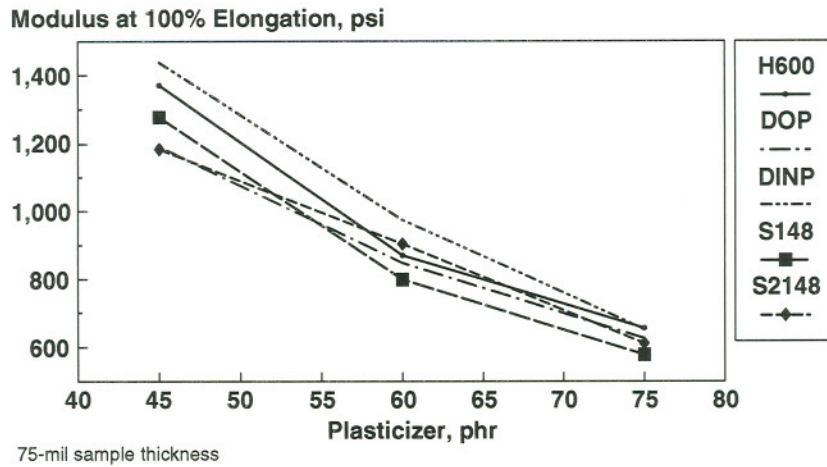
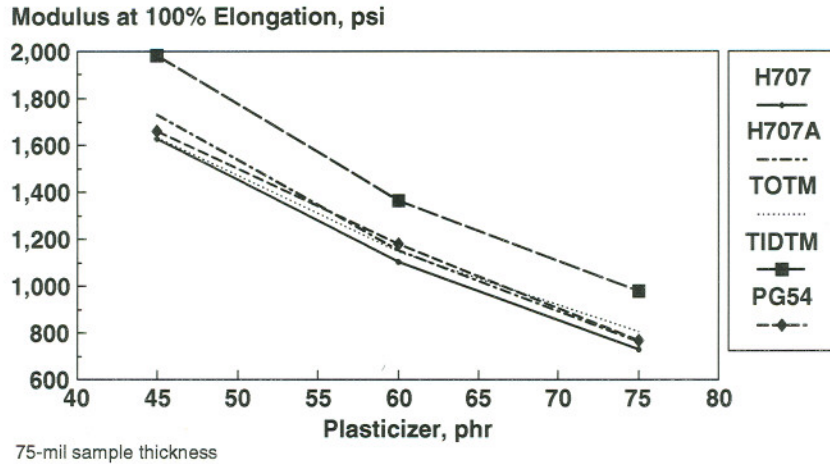
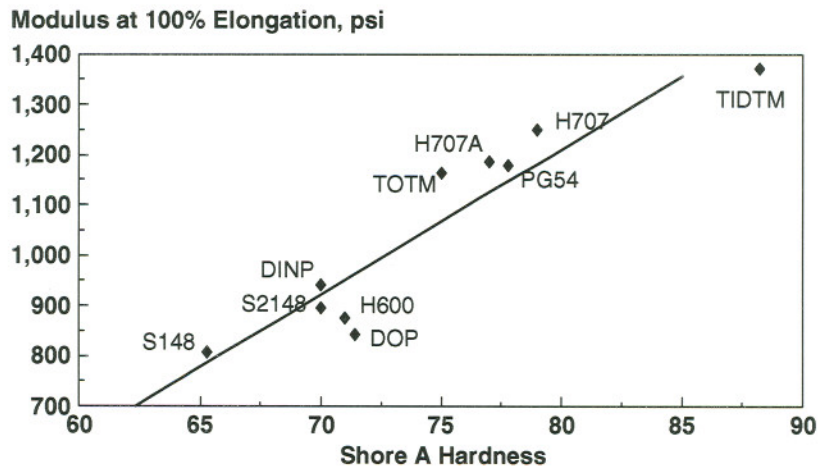


Figure 8
Tensile Modulus at 100% Elongation vs Plasticizer Level in Molded PVC



Shore A hardness values (ASTM D 2240) were determined for PVC molded specimens containing 60 phr of 10 different plasticizers using a Durotronic 1000 durometer. Figure 9 is a plot of the 100% elongation modulus vs the initial maximum indentation Shore A hardness. The softening efficiency of H600 is excellent, very similar to that of DOP, DINP, and S2148. H707 and H707A have similar efficiency to TOTM and PG54, all of which are more efficient than TIDTM.

Figure 9
Tensile Modulus at 100% Elongation vs Shore A Hardness for PVC With 60 phr Plasticizer

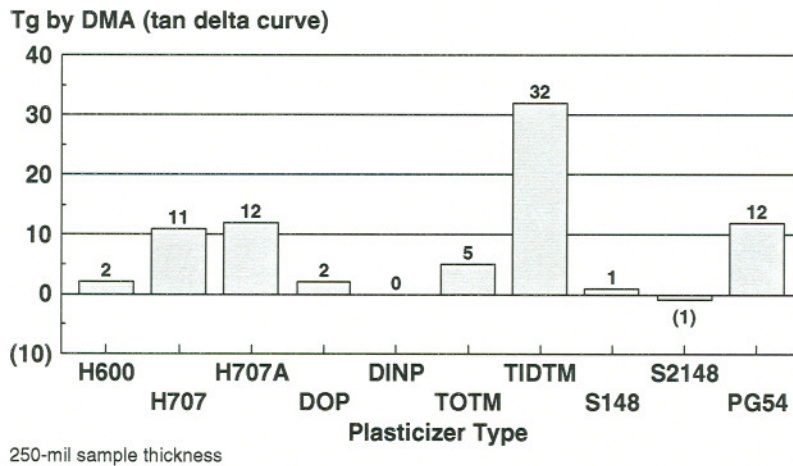


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The glass transition temperature (T_g) of a polymer is a measure of the temperature at which a material begins to relax or soften and is thus another measure of softening efficiency. At the same plasticizer level, a material with a lower T_g would indicate higher softening efficiency than one with a higher T_g. Figure 10 shows the T_g obtained by DMA vs plasticizer type of molded PVC specimens containing 60 phr plasticizer. The results parallel the trend observed in Figure 9. The order of softening efficiency from most to least efficient is:

S2148 ~ S148~DINP~H600~DOP>TOTM>H707A~H707~PG54>>TIDTM

Figure 10
T_g by DMA vs Plasticizer Type in PVC With 60 phr Plasticizer



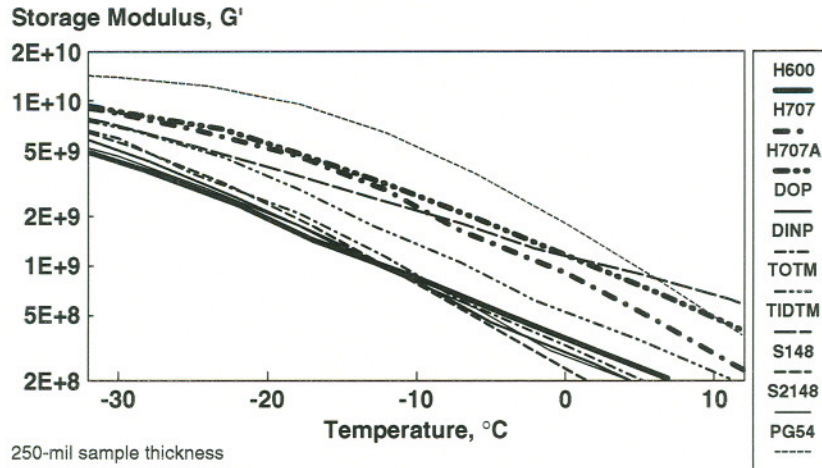
Low-Temperature Performance

Low-temperature performance of molded PVC specimens prepared with 60 phr of 10 different plasticizers was measured by two separate methods:

1. Dynamic mechanical analysis (DMA) from -50°C to 50°C to obtain the storage modulus or stiffness of each formulation as a function of temperature
2. Measurement of the brittle point by ASTM D 746

Figure 11 shows modulus (by DMA) vs temperature from -30°C to 10°C for molded PVC containing 60 phr of 10 different plasticizers. At these low temperatures, PG54 is by far the stiffest and most brittle plastic. Some crossovers occur as the temperature increases. Above -10°C, the modulus of the H600 formulation increases above that of the Santicizers (S148 and S2148) and the phthalates (DOP and DINP). Above -10°C, the modulus of TIDTM begins to cross over some of the others, and, by 10°C, has the highest modulus of all the formulations tested.

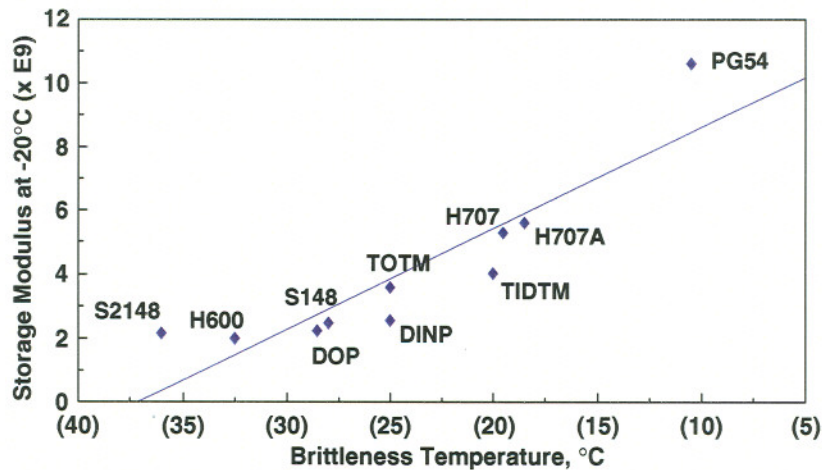
Figure 11
Storage Modulus vs Temperature for PVC With 60 phr Plasticizer



The brittle point (ASTM D 746) of a material is a measure of the temperature at which 50% of the samples exhibit brittle failure under specified impact conditions. Storage modulus at -20°C is plotted against the brittle point for molded PVC samples containing 60 phr of 10 different plasticizers in Figure 12. This chart reveals a general trend in low-temperature performance, with the best performers having the lowest brittle point and storage modulus:

S2148<H600<DOP~S148<DINP=TOTM<TIDTM~H707~H707A<<PG54

Figure 12
Storage Modulus at -20°C vs Brittleness Point for PVC With 60 phr Plasticizer



Product Safety

Read and understand the Material Safety Data Sheets (MSDSs) before using these products.

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