

Performance of Di-*n*-Hexyl Phthalate in Flexible Vinyl Formulations

RICHARD R. KOZLOWSKI and THOMAS K. GALLAGHER

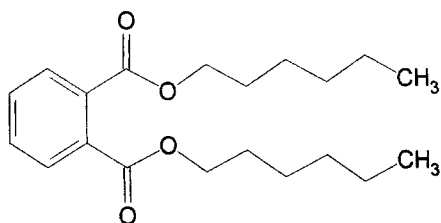
*Aristech Chemical Corp.
Pittsburgh, Pennsylvania 15225*

Low-molecular-weight esters have been available to the PVC compounder for many years. They have found a significant niche in the performance vs. permanence compromise as a compound ingredient that provides manufacturing efficiency or some special property with adequate permanence for many vinyl applications. In many respects, low-molecular-weight esters are the processing aids of the plasticizer family. This group of plasticizers may be said to include C₄ to C₇ dialkyl phthalates, the benzyl phthalates and the benzoic acid esters. This paper will introduce and compare di-*n*-hexyl phthalate (DNHP) to other phthalates against which it will directly compete.

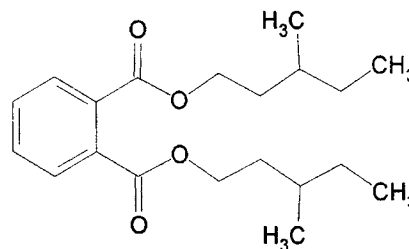
INTRODUCTION

Industrial alcohols in the C₄ to C₁₃ molecular weight range are widely used as plasticizer feed stocks. These feed stocks yield products of similar yet distinctive properties. Most studies of plasticizer performance (1, 2) have identified the structure of the alcohol as a key factor in the performance of the resultant ester plasticizer.

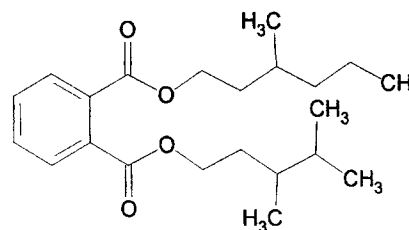
Di-*n*-hexyl phthalate is produced from linear hexyl alcohol.



DNHP
Di-*n*-hexyl Phthalate



DHP
Diisohexyl Phthalate



DIHP
Diisooheptyl Phthalate

Oxo Process six- or seven-carbon chain, branched phthalate plasticizers, such as diisohexyl phthalate (DHP) and diisooheptyl phthalate (DIHP), have at least one and many times multiple methyl branches attached to the main carbon chain.

PVC can be visualized as an entangled mass of stiff polymer chains. Plasticizers function by reducing the interchain bonding and expanding the distance be-

tween the polar sites on the resin chains, thus allowing the chains greatly increased freedom of motion. This results in increased extension, softness, and impact resistance. The polar part of the plasticizer molecule provides the solvent power while the nonpolar part confers other properties, such as flexibility (3). It is easy to propose that a linear molecule has fewer sites of rotational interference than a branched molecule. Thus a linear plasticizer will produce a PVC compound with more extensibility at equal loadings. Practical experience confirms this model, as it is generally recognized that the linear alcohol plasticizers are more efficient than branched alcohol esters in producing the desired plasticizing effects (4). The data that follow show that linear hexyl phthalate demonstrates the same performance advantages that other linear plasticizers show over their branched counterparts. The data show that DNHP can provide equivalent or superior PVC compound performance as an alternative to DHP or DIHP.

EXPERIMENTAL

Dispersion Resin Tests

Plastisol Preparation

Plastisols were prepared by using the following formulation:

Dispersion Resin (IV = 1.2)	100 parts
Plasticizer	75 parts
Stabilizer, Liquid Barium-Zinc	2.5 parts

The liquid plasticizer and stabilizer were mixed separately by hand then 60% of this mixture was added to the resin in the mixing bowl of a planetary gear mixer (Hobart Model N-50). The plastisol was mixed at low shear for 20 minutes, stopping to insure complete addition of ingredients. The remaining liquid was then added, and mixing was continued for an additional 10 minutes. The plastisol was deaerated in a desiccator, evacuating for 30 minutes after the collapse of the foam.

Fusion Properties

Hot Bench Gel Test: The hot bench gel temperature of the prepared plastisol was measured according to SPI-VD-T18. A small amount of plastisol was poured onto an aluminum thermal gradient plate and then drawn into a 6-mil film. The gel temperature, determined by using a pyrometer, is defined as the temperature at which the film begins to adhere to the plate.

Cone and Plate Fusion Temperature: The fusion temperature of the plastisol was determined by measuring the peak viscosity of the plastisol when heated in a cone and plate viscometer. The plastisol was heated from 50 to 200°C at 10°C/min.

Brabender Fusion Curves: The processing characteristics were measured using a Brabender Torque Rheometer, Model PL-2100, equipped with a No. 6 mixing head. Fifty milliliters of the plastisols were injected

into the mixing head under two conditions. The apparent gel temperature was measured by increasing the mixer head temperature 2°C/min from 50 to 190°C according to SPI-VD-T23. The fusion time was measured at a constant bowl temperature of 115°C in a second run.

Plastisol Volatility

Thirty-gram samples of the plastisols were placed in 100-mm Petri dishes and placed in an air-circulating oven set at 190°C (375°F). The weight loss was measured after 10, 20 and 30 minute exposure.

Plastisol Viscosity

Low Shear Viscosity: The viscosity of the prepared plastisol was tested by using an LV Brookfield viscometer at 23°C, using Spindle #4 @ 60 rpm after two hours; 24 hours; 3, 7, 14 and 28 days, according to ASTM D 1824.

High Shear Viscosity: The viscosity of the plastisol was tested by using a Burrell-Severs viscometer at 23°C after 24 hours according to ASTM D 1823.

Mechanical Properties of Plastisols

Samples were prepared by casting the plastisol into 20-mil thick films and fusing at 190°C for 10 minutes. The tensile properties were determined by using a Tinius Olsen Model 2000 Universal Tester according to ASTM D 638. The Shore A hardness was measured by layering 1.5 × 2 inch square plaque samples and measuring the hardness after 10 seconds according to ASTM D 2240.

Low Temperature Properties

Brittleness Temperature: Fifty-mil test plaques were prepared by compression molding the plastisol for 3 minutes at 190°C. The low temperature impact resistance was tested according to ASTM D 746 by using a Tinius Olsen Brittleness Tester.

Low Temperature Flexibility: The Clash-Berg temperature was determined on 50-mil test plaques according to ASTM D 1043 by using a Tinius Olsen Torsional Stiffness Tester.

Suspension Resin Tests

Powder Mix Time

The dry blend times of the plasticizers were compared by testing them according to ASTM D 2396.

PVC Resin—Fish Eye (Gel) Test

The following formulation was used for the fish eye (gel) test:

Suspension Resin (IV = 1.02)	65 parts
Stearic Acid	0.3 part
Plasticizer	39 parts
Stabilizer, Liquid Barium-Zinc	2.5 parts
Black Dispersion (5%)	0.1 part

Table 1. Properties of Plasticizers.

	DNHP	DHP	DIHP	DOP
Specific Gravity @ 25/25°C	1.002	1.003	0.992	0.983
Viscosity @ 25°C, cps	22	33	47	57
Volatility, % (1 Hr. @ 110°C)	1.5	3.1	1.4	1.0
Solubility Parameter	9.11	8.97	8.85	8.87
Plasticizer Solution Temperature, °C	96	100	110	116

Solid and liquid ingredients were hand-mixed separately. The liquid ingredients were added to the dry hand-mixed ingredients and the mixture was immediately placed on a two-roll mill. The compound was milled at 149°C for 4 minutes, folding edges only once at one-minute intervals. The mill sheet was removed, allowed to cool and placed on a back-lighted surface. Gels/unit area were counted under magnification.

Plasticizer Solution Temperature

A few grains of resin were placed in a pool of plasticizer on a Fisher-Johns melting point apparatus. The temperature was ramped at 5°C/min, and the penetration of plasticizer into the resin was visually observed. The solution temperature is defined as the temperature at which all resin particles have solvated and may be called the clear point.

RESULTS AND DISCUSSION

Branched hydrocarbons typically show higher viscosities and volatilities than the linear isomers of the same molecular weight. Similarly, viscosity usually increases with molecular weight while volatility or vapor pressure decreases. Table 1 shows both of these effects for phthalate esters. DNHP has a lower viscosity than DHP while DIHP and DOP are higher, as expected.

Volatility also follows the predicted pattern. DHP is the most volatile, followed by DNHP, DIHP and DOP. We can also see that the linearity of DNHP has the positive effect of overcoming the molecular weight advantage of DIHP, showing nearly equivalent weight loss.

One theoretical estimate of polymer-plasticizer compatibility is the solubility parameter (δ). The theory proposes that polymer-plasticizer combinations of similar δ will be compatible and form miscible systems over a large concentration range.

One method of estimating the solubility parameter of resins and solvents was developed by Small (5). By using this computational method the δ of PVC resin is estimated to be 9.66. The data in Table 1 show that DNHP has a δ closer to PVC than the other low-molecular-weight phthalates and should be the most compatible and efficient plasticizer of this family. The plasticizer solution temperature as shown in Table 1 supports this conclusion. DNHP has a substantially lower solution temperature than DIHP and DOP. Therefore, DNHP should have the processing performance of DHP and the volatility performance of DIHP.

Fusion Temperature Measurements

Low-molecular-weight phthalates are typically chosen by the compounder for their ability to improve the processing characteristics of the formulation. This characteristic can be important to both dispersion and suspension resin compounders. Improved processing for plastisol compounders generally means a need to produce parts at shorter oven residence times or at lower oven temperatures or both. Table 2 compares DNHP under varying test conditions in plastisols.

Hot Bench Gelation Temperature (SPI-VD-T18): This test shows that DNHP is a slightly faster fusing plasticizer than DHP. Both are faster fusing than DIHP or DOP.

Table 2. Gelation and Fusion Data of Plasticizers.

	DNHP	DHP	DIHP	DOP
Hot Bench Gelation (°C)	63	64	68	71
Cone & Plate Viscosity Test				
Onset Temperature	73	77	79	83
Fusion Temperature (°C)	125	127	135	140
Isothermal Brabender Test @ 115°C				
Time to Fusion (sec)	44	62	180	352
Maximum Torque (N-m)	13.3	13.9	13.0	10.0
Temperature Programmed Brabender Test (50–190°C)				
Onset Temperature (°C)	70	70	75	86
Fusion Temperature (°C)	119	119	124	135
Maximum Torque (N-m)	13.7	11.8	9.4	9.7

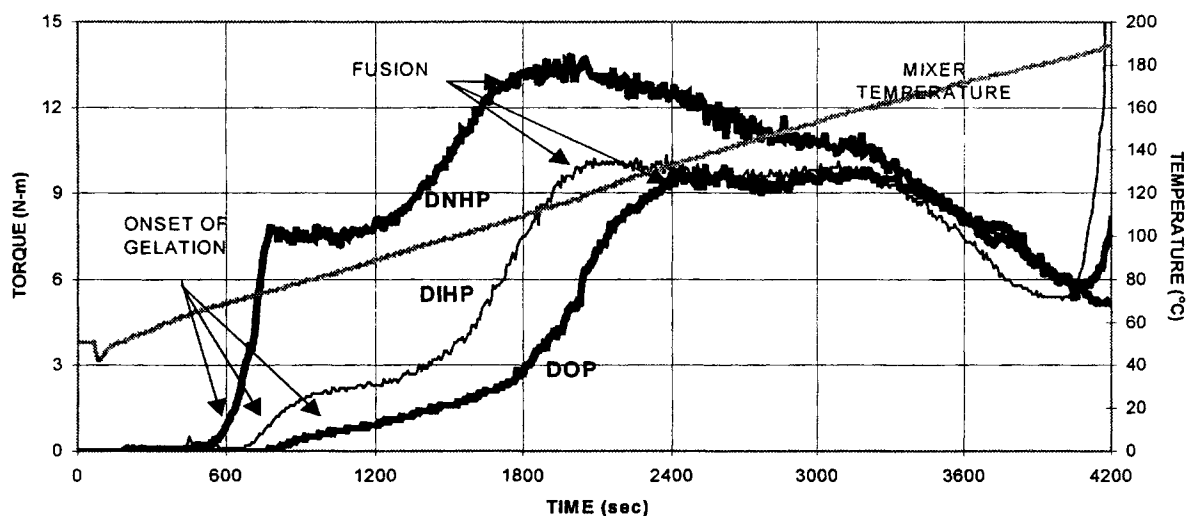


Fig. 1. Temperature-programmed Brabender fusion curve.

Cone and Plate Viscosity: Plastisol fusion characteristics can be measured by monitoring the viscosity response to a programmed temperature rise of 10°C over a range of 50°C to 190°C. The gelation onset temperature is defined as the point at which viscosity begins to increase rapidly. The point of maximum viscosity is defined as the completion of gelation or the minimum fusion temperature. The results displayed in Table 2 support the idea that DNHP fuses slightly faster than DHP.

Brabender Tests: In an isothermal test run at 115°C, the time to fusion was measured. Again, Table 2 shows that DNHP is slightly faster than DHP and substantially faster than both DIHP and DOP.

When the temperature programmed test is performed according to SPI-VD-T23, the difference between DNHP and DHP is not seen. The torque curve of DHP is essentially identical to the curve of DNHP displayed in Fig. 1. This may be due to the low viscosity

of the plastisols. The instrument may not be sensitive enough to detect the slight increase in the viscosity. The onset temperature is defined as the temperature when the torque begins to increase. The fusion temperature is the point where the torque reaches maximum. Both hexyl phthalates are lower than DIHP and substantially lower than DOP, as listed in Table 2.

It is generally recognized that lower-molecular-weight phthalates are more solvating than higher-molecular-weight phthalates. This would explain the lower fusion temperature and faster fusion times of both DNHP and DHP compared to DIHP and DOP.

In comparison of higher-molecular-weight phthalates, the linear isomer usually shows a higher fusion temperature (6). The slight improvement in fusion temperature and/or fusion time of DNHP over DHP was not expected. The effect seen may be due to the lower viscosity of the linear DNHP, allowing it to penetrate and solvate the resin particles more quickly than the

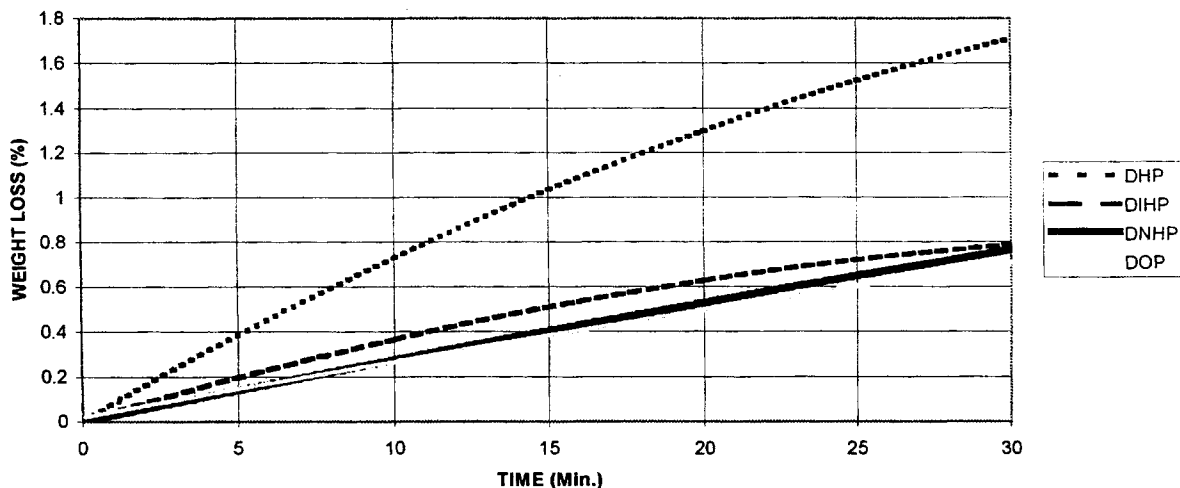


Fig. 2. Plastisol volatility @ 190°C (375°F).

Table 3. Brookfield Viscosity of Plastisols.

LVT Spindle #4 @ 60 rpm	DNHP	DHP	DIHP	DOP
Initial, cps	2080	2370	2360	3060
24 hour, cps	3040	3270	3240	4330

branched DHP. In addition, the higher solubility coefficient of DNHP may account for the differences measured in the fusion tests.

Plastisol Weight Loss

The volatility of the plastisol during processing is closely related to the volatility of the plasticizer. The data (Fig. 2) show that DNHP produces a plastisol with reduced weight loss compared to DHP at typical processing temperatures. This suggests reduced processing emissions might be experienced.

Plastisol Viscosity

One of the most important factors in the initial viscosity of a plastisol is the viscosity of the plasticizer. Table 3 shows both the initial and 24-hour viscosity of the plastisols. An analysis of the data in the table shows that the linear DNHP yields an initial Brookfield viscosity that is 10% to 20% lower than that of the branched phthalates DHP or DIHP. Ultimately, the solvating power of DNHP yields a plastisol with a viscosity similar to that of DHP or DIHP (Fig. 3). The intermediate shear viscosity as measured by a Severs viscometer shows that the effect of linearity is even greater (Fig. 4). The Severs viscosity of the DNHP-containing plastisol is over 20% less than that of DHP and 30 to 40% less than that of DIHP.

Mechanical Properties

After the processing differences are assessed, the compounder must be sure that the performance of the part produced will meet standards. Table 4 lists the effects of DNHP on the mechanical properties of cast 20-mil films of plastisols. Both the modulus @ 100% elongation and the Shore A hardness results indicate that DNHP is slightly more efficient than DOP at equal parts.

Low Temperature Properties

Linear phthalate plasticizers have always been shown to improve the low temperature performance of vinyl compounds. This is true of DNHP. Figure 5 illustrates that the linear structure of DNHP improves the Clash-Berg temperature (ASTM D 1043) and the brittleness temperature (ASTM D 746) by at least 7°C at 75 phr loading.

Suspension Resin Properties

PVC Resin Solvency: According to the ASTM test method D 2396 for powder mix dry up time, DNHP is slightly more solvating than branched DHP and measurably more solvating than either DIHP or DOP (Fig. 6). The results correlate well with the dispersion resin tests reported above.

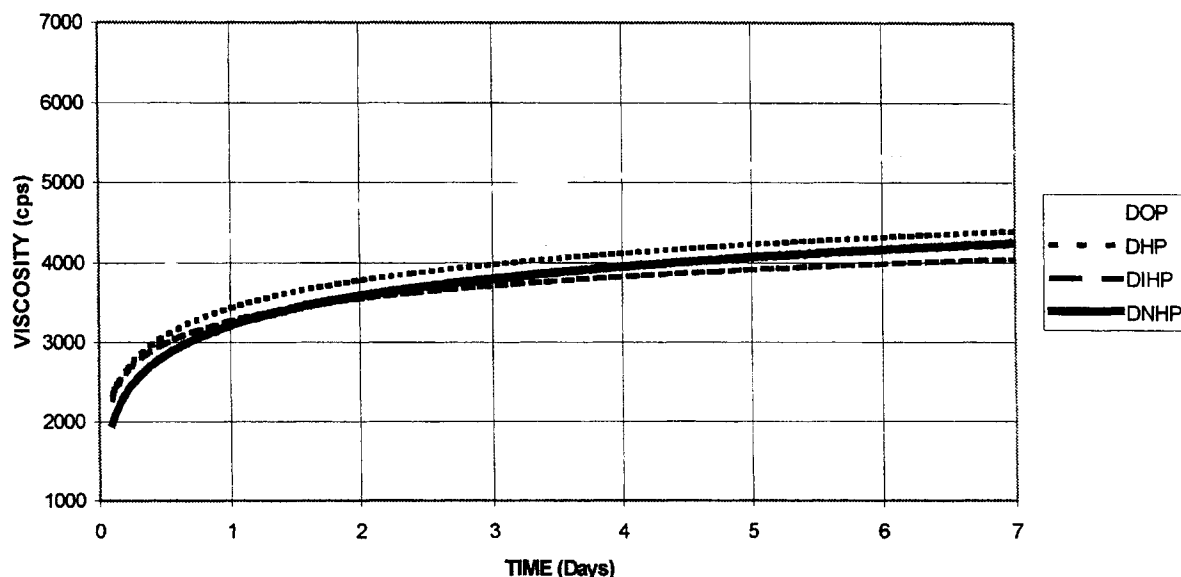


Fig. 3. Brookfield viscosity of plastisols.

Performance of Di-n-Hexyl Phthalate in Flexible Vinyl Formulations

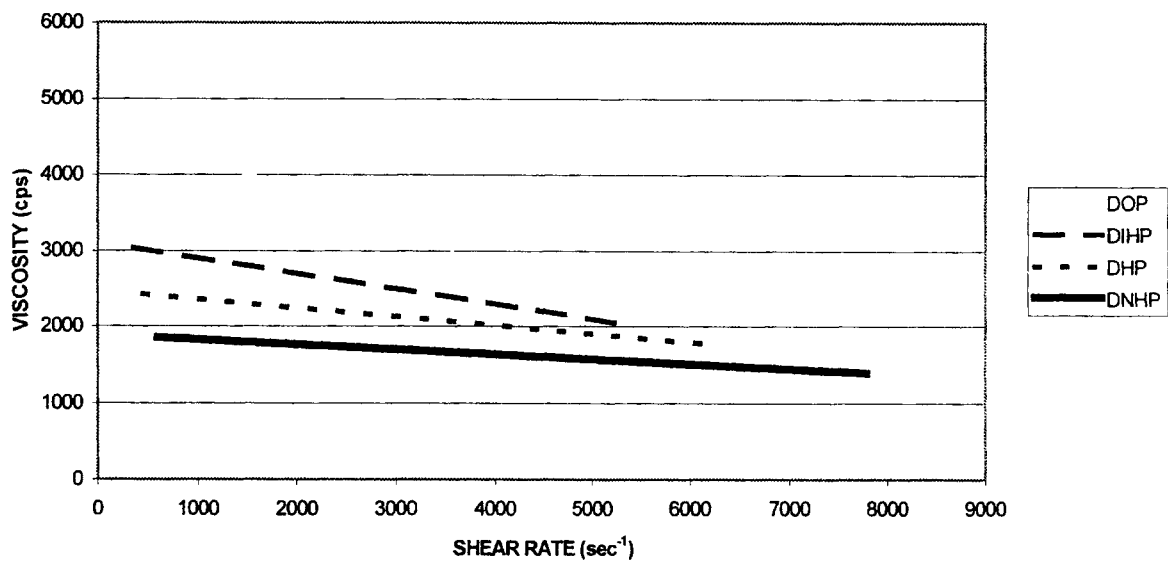


Fig. 4. Severs viscosity of plastisols.

Table 4. Mechanical Properties @ 75 phr.

	DNHP	DHP	DIHP	DOP
Tensile Strength, psi	2265	2275	2465	2400
Ultimate Elongation, %	500	470	480	460
Modulus @ 100% Elongation, psi	650	665	720	755
Hardness, Shore A (10 sec. Dwell)	62	63	64	65

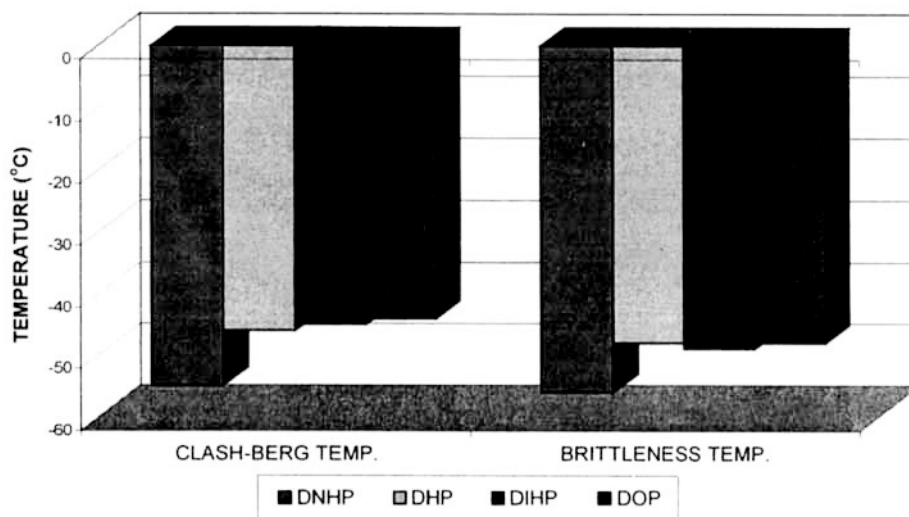


Fig. 5. Low temperature properties.

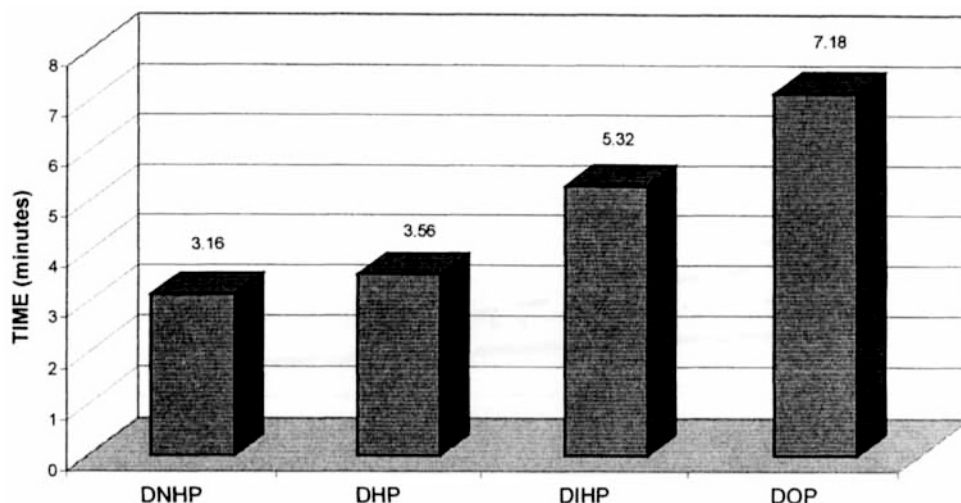


Fig. 6. Powder mix time of lower-molecular-weight phthalates.

Table 5. Fish Eye Gel Test.

Plasticizer	DNHP	DIHP	DOP
No. of Gels	5.3	8.6	46.0

PVC Resin Fish Eyes: The test was developed to measure resin quality by estimating the number of hard unplasticized particles remaining in a poorly processed compound. If the emphasis is placed on plasticizer effect, the method can be used to measure the effect of plasticizer structure on gel reduction. Table 5 shows these data. High solvating plasticizers do provide early penetration of hard resin particles and agglomerates. The films do show reduced levels of gels. DNHP is the most effective plasticizer in this group of phthalates.

CONCLUSION

The data developed in this paper suggest that DNHP expands the range of performance for the family of low-molecular-weight phthalates. Based on a linear C₆ alcohol, DNHP provides several improved plasticizer properties. It offers the fusion characteristics of a branched hexyl phthalate with the volatility of a higher-molecular-weight heptyl phthalate. This will give many PVC processors the ability to lower operating temperatures and/or increase line speeds by replacing the higher-molecular-weight DIHP. This re-

placement should not cause a significant increase in fuming or weight loss during processing. In addition, a lower initial plastisol viscosity can be achieved by using DNHP. This could again lower processing emissions by reducing the amounts of diluents and viscosity reducers used in plastisol formulations. Finally, the improved low temperature flexibility of a linear plasticizer will bring additional improvement to the final compound performance.

ACKNOWLEDGMENTS

We would like to thank Aristech Chemical Corporation for their support in preparing and publishing this paper. We would especially like to thank Paul Klaus, Mike Elliot, Regis Ryan and Keith Borden for their assistance. Also, we wish to thank Shirley A. Moy and her staff at Condea Vista for their work in supplying us with the powder mix dry up data.

REFERENCES

1. J. K. Sears, J. R. Darby, *The Technology of Plasticizers*, John Wiley and Sons, New York (1982).
2. L. Meier, *Plastics Additives Handbook*, R. Gachter and H. Muller, ed.; Oxford University Press, New York (1990).
3. E. K. Baylis, *Plasticisers, Stabilisers, and Fillers*, p. 139, P. D. Ritchie, ed.; Iliffe Books, London (1972).
4. L. G. Krauskopf, *Handbook of PVC Formulating*, p. 180, E. J. Wickson, ed.; John Wiley and Sons, New York (1993).
5. P. A. Small, *J. Appl. Chem.*, **3**, 76 (1953).
6. L. G. Krauskopf, *Encyclopedia of PVC*, p. 214, L. I. Nass, ed.; Marcel Dekker, New York (1988).