

# Physical Properties of Cured Plastisols Having Alicyclic Alcohol Esters as Plasticizers

T. H. G. MICHAEL AND F. J. McQUAIG  
Howards & Sons (Canada), Ltd., Cornwall, Ontario, Canada

Esters of cyclohexanol and methylcyclohexanol are used as plasticizers for nitrocellulose and poly(vinyl chloride), but little data describing the specific properties they impart have been published. The purpose of this work was to determine the behavior of a number of these esters when used as the dispersing medium for poly(vinyl chloride) in the plastisol technique.

The data given indicate that they contribute high tensile strength, excellent oil resistance, and a high degree of permanence; however, low temperature flexibility is not outstanding. These properties make the plasticizers useful for applications requiring such features.

The dibasic acid esters of alicyclic alcohols (most commonly, cyclohexanol and methylcyclohexanol) are used as plasticizers for various materials, including nitrocellulose and poly(vinyl chloride). Little data have been published to show the specific properties imparted to poly(vinyl chloride) by these esters, but Buttrey (4) and Petzold (8) quote a limited amount for dimethylcyclohexyl phthalate in PVC compositions; Reed and Harding (9) include some for dicyclohexyl phthalate and for dimethylcyclohexyl phthalate; Doolittle (6) gives some data for dicyclohexyl phthalate, but not for the methyl derivative. The same is true of Lawrence and McIntyre (7). The compositions examined by all these authors were prepared by calendaring. As far as is known, no results have been published showing the behavior of the alicyclic alcohol esters in plastisols.

The purpose of this study was to determine the behavior of a number of these esters when used as the dispersing medium for poly(vinyl chloride) using the plastisol technique. Esters of the acids, phthalic, adipic, azelaic, sebacic, isosebacic, and oxalic were used with a series of 2-ethylhexanol esters selected for comparison purposes because they are widely used in plastisol compounding (Table I). The following esters were prepared in this laboratory:

1. Dimethylcyclohexyl isosebacate (SIS). This ester of methylcyclohexanol was prepared from isosebacic acid supplied by U. S. Industrial Chemicals (10). The acid consists of about 80% of  $\alpha$ -ethylsuberic acid, with about 10% each of sebacic acid and  $\alpha$ -diethyladipic acid. The esterification was carried out in a 2-liter glass flask, using an excess of methylcyclohexanol. Half gram-equivalent quantities were used. Concentrated sulfuric acid (2 ml. of 50% by wt.) as a catalyst, and benzene as entraining solvent were added. The reaction was carried out at 115°C., and on its completion, judged by acidity below 0.3%, the unreacted acid was removed by washing with 2N sodium hydroxide.

The benzene and excess alcohol were distilled off under reduced pressure, the product treated with decolorizing carbon, and filtered.

2. Di-2-ethylhexyl isosebacate (DOIS). Prepared as described, except that the alcohol, 2-ethylhexanol, was used.

3. Dimethylcyclohexyl azelate (SZ). Prepared by a method similar to that described, but using commercial azelaic acid instead.

4. Dicyclohexyl azelate (DCHZ). Prepared as described using cyclohexanol and commercial azelaic acid.

## PREPARATION OF PLASTISOLS

The following basic formulation was used in preparing the plastisols:

	Pts./Wt.
poly(vinyl chloride) resin Geon 121	100
plasticizer	70
stabilizer	4
pigment TiO <sub>2</sub>	10
lead stearate	4
Titanox RA	10

The ingredients were thoroughly hand mixed, then given three passes through a 3-roll laboratory mill.

For dicyclohexyl phthalate and dimethylcyclohexyl phthalate, the viscosities resulting from this formulation were too high to be workable. Consequently, the mixture was thinned with a solution of diisobutyl ketone and mineral spirits, the former in the ratio of 35:140 and the latter in the ratio of 10:20.

Other plastisols were also prepared: one containing dimethylcyclohexyl phthalate and di-2-ethylhexyl phthalate in the ratio by weight of 1:2; and two in which a part of the Geon 121 was replaced by Resin MS2, a condensed cyclic ketone resin, used as a viscosity stabilizer and depressant. The plasticizer used in the latter pair of plastisols was dimethylcyclohexyl adipate.

Subsequent to preparation, viscosity determinations using a Brookfield viscometer were made both after one hour and after eight days (Table II). The viscosities of the plastisols containing dimethylcyclohexyl adipate and Resin MS2 are also shown in Figure 1.

For most of the tests, samples were prepared by casting sheets in a stainless steel 8 x 10 inch mold and curing these for 15 minutes at 185°C. The thickness of the cured sheets was about 8 mil. Test pieces for low temperature flexibility were cut from pieces prepared in a 4 1/2 x 2 1/2 x 1/8 inch mold and cured according to the same schedule. To eliminate trouble from bubble formation, the

**TABLE I. PROPERTIES OF MATERIALS USED**

Plasticizer	Abbreviation	Source	Boiling Range		Sp. Gr., 20° C./20° C.	Viscosity, Cps., 25° C.	N <sub>20</sub> D
			° C.	Mm. Hg			
Dicyclohexyl phthalate <sup>a</sup> (m.p., 63° C.)	DCHP	Howards	..	..	..	..	..
Dimethylcyclohexyl phthalate <sup>a,b</sup> (m and p, isomers)	SP	Howards	250	2	1.075	11,600	1.516
Di-2-ethylhexyl phthalate	DOP	Monsanto	290	50	0.986	55.5	1.485
Dimethylcyclohexyl adipate <sup>a,c</sup>	SA	Howards	190-200	3	1.007	35.6	1.468
Di-2-ethylhexyl adipate <sup>a</sup>	DOA	CR&C	232	10	0.927	15	1.446
Dimethylcyclohexyl sebacate <sup>d</sup> (m and p isomers)	SS	Howards	210-220	2	0.984	72	1.469
Di-2-ethylhexyl sebacate <sup>a</sup>	DOS	Hardesty	248	4	0.910	20	1.447(28° C.)
Dimethylcyclohexyl isosebacate	SIS	lab.	285	0.5	0.973	56	1.466(25° C.)
Di-2-ethylhexyl isosebacate	DOIS	lab.	170-200	5.5	0.915	21	1.449
Dicyclohexyl azelate	DCHZ	lab.	200-210	6	1.005	50	1.471
Dimethylcyclohexyl azelate	SZ	lab.	208-215	6	0.988	46.5	1.468
Di-2-ethylhexyl azelate <sup>a</sup>	DOZ	CR&C	237	5	0.918	21	1.446
Di-(dimethylcyclohexyl) oxalate <sup>a,e</sup> (m.p., -25° C.)	BB	Howards	180-200	4	1.012	54.1	1.467
Resin MS2 (condensed cyclic ketone) (m.p., 85-95° C.)		Howards			1.078		

<sup>a</sup> Used without further purification.  
<sup>b</sup> Trade-name, Sextol Phthalate.  
<sup>c</sup> Trade-name, Sextol Adipate.

<sup>d</sup> Trade-name, Sextol Sebacate.  
<sup>e</sup> Trade-name, Barkite B.

plastisol was poured directly into this mold after passing over the roll mill.

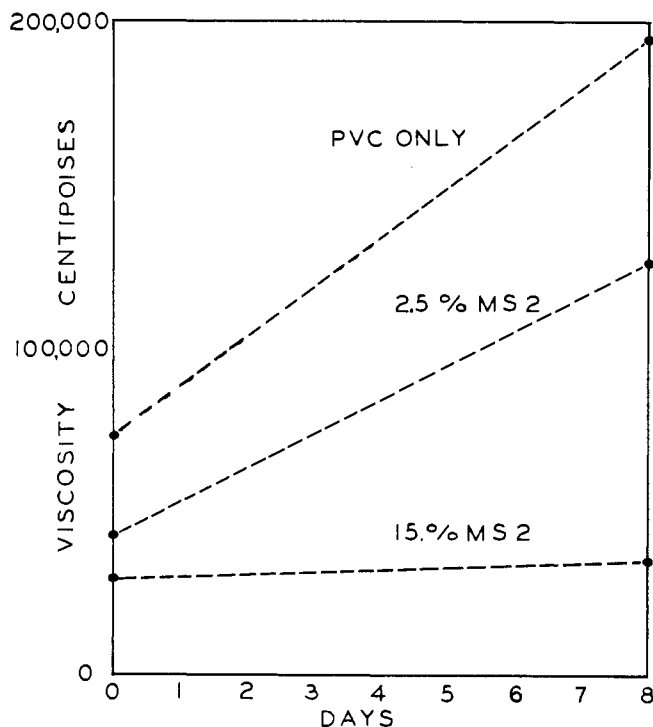
**DESCRIPTION OF TESTS**

Tensile strength (Table III). This test was carried out on a Scott pendulum type tensile strength tester, Model L6, having a speed of jaw separation of approximately 20 inches per minute. Test pieces were cut from the cured sheets by means of a steel die, having dimensions of 4.0 x 1.0 inch. Thicknesses were measured with a micrometer, and the elongation was measured by the procedure described under Method A in ASTM Specification D882-49T (2). The tensile strength was determined under four conditions:

1. At +70° F. and 50% R.H. after conditioning under these same conditions.
  2. At - 20° F. after conditioning at +70° F. and 20% R.H.
  3. At - 70° F. after conditioning at +70° F. and 20% R.H.
  4. After exposure in an Atlas single-arc Weatherometer, used without water spray, for 250 hours and followed by conditioning at +70° F. and 50% R.H.
- The cold box used for the low temperature determinations

**TABLE II. VISCOSITIES OF PLASTISOLS**

Plasticizer	Viscosity, Centipoises, Brookfield 5/6	
	After 1 hour	After 8 days
DOP	63,000	100,000
SP/DOP 1/2	76,000	145,000
SA	74,000	194,000
DOA	34,000	36,000
DCHZ	113,000	> 200,000
SZ	64,000	113,000
DOZ	23,000	26,000
DCHS	45,000	> 200,000
SS	34,000	54,000
DOS	21,000	32,000
SIS	35,000	66,000
DOIS	13,000	24,000
BB	27,000	67,000
SA - Resin MS2, 2.5%	43,000	126,000
SA - Resin MS2, 15%	30,000	36,000



**Figure 1. Viscosities of plastisols containing Sextol Adipate with and without Resin MS2**

TABLE III. ELONGATION AND TENSILE STRENGTH

(Av. of about 10 determinations)

Plasticizer	+70° F.		-20° F.		-70° F.		After 250 Hours Weatherometer Exposure	
	%	Lb./sq.inch	%	Lb./sq.inch	%	Lb./sq.inch	%	Lb./sq.inch
SP	175	3100	0	8100	0	10600	135	3450
DOP	176	1190	43	2310	24	3930	64	720
SP/DOP 1/2	260	2140	33	3230	7	4400	138	1520
SA	199	1590	48	2360	15	4880	168	1530
DOA	168	1120	96	1940	41	2700	171	1240
DCHZ	192	1280	68	2180	13	4130	253	2000
SZ	265	1940	38	2970	9	4620	219	1860
SS	129	930	48	1550	8	3850	63	670
DOS	105	740	84	1190	15	2140	93	690
SIS	40	460	0	1250	0	1320	40	480
DOIS	practically nil							
SA/MS2,2.5%	197	1140	21	2950	0	4300	190	1600
SA/MS2,15%	270	1080	40	2440	0	4020	186	1070

consisted of a chamber, 2 inches in diameter x 12 inches in height, completely surrounded by a jacket 1 1/2 inches thick.

It was constructed of galvanized steel and insulated from the atmosphere by a 2-inch cork layer. The jacket was closed at the bottom and open at the top. The inner chamber was also closed at the bottom except for a hole of just sufficient diameter to allow the rod supporting the lower clamp to move freely. The open tops were covered with a cork cover during operation. The cold box was split down the middle, so that it could be opened for the insertion of specimens. Powdered dry ice was packed into the jacket as coolant. A thermometer was inserted through the cork top so that its bulb top was on a level with the lower edge of the upper clamp. Cold dried air, chilled by passing through a tower packed with dry ice, was blown into the test chamber.

Oil Extraction (Table IV). Test pieces approximately 1 x 3 inches, cut from the cured sheets, were immersed in light mineral oil (Parfinol, sp. gr. 0.870) for 24 hours at 50° C., and, after removal, were wiped clean of excess oil, rinsed in petroleum ether, and dried. The samples were conditioned for three hours at 50° C. before each weighing to determine weight loss.

Water extraction and absorption. Test pieces approximately 1 x 3 inches, cut from the cured sheet, were accurately weighed and extracted in distilled water under reflux in individual flasks for 24 hours. Then they were removed, washed in cold distilled water, wiped dry, reweighed, and suspended in an oven at 100° C. for 24 hours, cooled, desiccated for one hour, and reweighed. The amount

of water absorbed and of matter extracted were calculated (Table IV).

Volatility. Weighed samples, 1 x 3 inches, cut from the cured sheet, were suspended in an oven for 96 hours at 100° C. and reweighed after desiccating. The percentage of volatile matter shown in Table IV, was calculated.

Migration loss. Discs having an area of 2.08 square inches, cut from the cured plastisol sheet, were weighed and placed completely in contact with a dried lacquer film under a weight of 350 grams for a period of 35 days. The test discs were then reweighed and the loss in weight calculated and reported as loss of plasticizer in Table IV. The lacquer films were allowed to dry for 14 days before use; their compositions were:

	Wt. %
Nitrocellulose, 1/2 sec. RS	38.8
Sextol phthalate	11.8
Dibutyl phthalate	14.2
Ester gum	35.2

Low temperature flexibility (Table V). This property was determined according to the method of Clash and Berg (5). It is also described in ASTM Method D1043-51 (3). The quantity, T<sub>4</sub>, described by Doolittle (6) was calculated from the experimental data. For the compounds dimethylcyclohexyl adipate, dimethylcyclohexyl isosebacate, and di-2-ethylhexyl adipate, the T<sub>4</sub> was determined for a plasticizer content of 60 and 80 parts/100 of resin, as well as the original 70 parts/100 of resin. These figures are:

TABLE IV. RESISTANCE PROPERTIES OF PLASTISOLS

Plasticizer	Oil Extraction, %	Water Absorption, %	Water Extraction, %	Volatility, %	Migration Loss, %
SP	2.0	23.7	3.5	4.9	3.1
DOP	28.0	21.8	3.8	7.5	1.0
SP/DOP	12.3	25.4	2.8	9.1	1.9
SA	16.6	25.4	8.5	12.3	2.0
DOA	30.1	21.1	6.7	13.5	5.8
DCHZ	20.4	12.2	4.1	6.6	0.8
SZ	19.2	22.9	3.1	5.6	0.0
DOZ	26.6	18.4	3.5	4.6	7.9
SS	21.0	27.2	2.9	3.2	0.4
DOS	24.7	16.8	3.0	4.1	6.2
SIS	28.6	17.3	2.6	3.1	0.2
BB	7.2	29.5	12.5	30.2	-
SA/MS2,2.5%	19.2	20.8	7.7	13.3	1.2
SA/MS2,15%	27.4	31.2	10.0	21.4	2.5

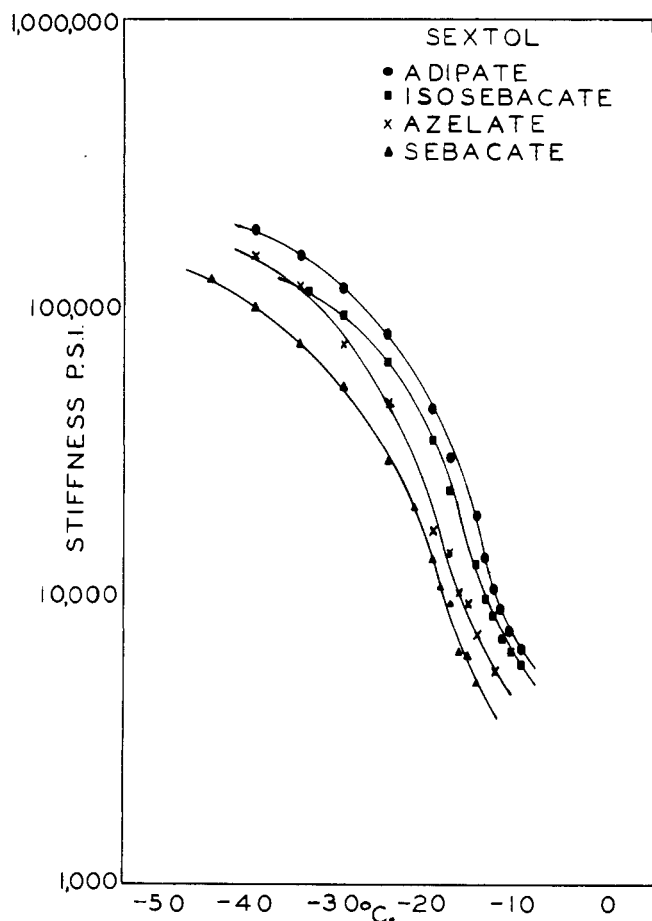


Figure 2. Stiffness-temperature curve for Sextol esters

Plasticizer	Plasticizer Conc., P.H.R.		
	60	70	80
	T <sub>4</sub> , °C.		
SA	-8	-12.5	-17.5
DOA	-35	-47	-54
SIS	-8	-14	-18

The stiffness-temperature curves have been prepared for the four methylcyclohexyl esters. These show the stiffness in pounds per square inch plotted as a function of temperature in Figure 2.

## DISCUSSION

The tensile strengths of the cured plastisols plasticized with alicyclic alcohol esters are generally much higher than those plasticized with 2-ethylhexanol esters. This appears true for all test conditions. SP gives the highest tensile strength, a property also evident in blends with DOP. The percentage elongation at break is equal or higher for methylcyclohexyl esters than for octyl esters, but it decreases more markedly at low temperatures. The tensile strength is little affected by Weatherometer exposure, although the percentage elongation is reduced. Oil extraction is much less for methylcyclohexyl esters than for the octyl esters, an effect particularly noticeable in the case of the phthalate. Cyclohexyl and methylcyclohexyl esters appear to have a very high degree of permanence, as shown by both the volatility and migration loss figures.

The low temperature behavior of the cyclohexyl and methylcyclohexyl esters is not so good as that of the octyl esters. Using the quantity T<sub>4</sub> as an index of low

TABLE V. LOW TEMPERATURE CLASH & BERG TESTS

Plasticizer	T <sub>4</sub> °C. <sup>a</sup>
SP	-5.8
DOP	-21
SP/DOP	-10
SA	-12.5
DOA	-47
DCHZ	-17.8
SZ	-16.5
DOZ	-43
SS	-18.5
DOS	-41
SIS	-14
DOIS	-38
BB	+2.0
SA/MS2, 2.5%	-14
SA/MS2, 15%	-17.5

<sup>a</sup> Temp. at which stiffness is 10,000 lb./sq. in.

temperature behavior, none of the methylcyclohexyl esters tested are as good as DOP. It should be noted, however, that the test was carried out under the short and arbitrary time of deflection, five seconds. Aiken and coworkers (1) have pointed out that plasticizers having a ring structure, when tested over a longer period, may be more effective than esters of a linear type.

Samples containing Resin MS2 had more stable and initially lower viscosities than the comparable formulation without it. Their behavior in other tests was consistent with a composition having a higher ratio of plasticizer to poly(vinyl chloride) resin than the control. Thus, according to the tests carried out, Resin MS2 appears inert. This is typified by the low temperature flexibility tests, which show a proportional drop in the T<sub>4</sub> temperature with an increase in Resin MS2 content.

It may be theorized that the somewhat bulky and unyielding cyclic ring structure of these plasticizers is responsible for these effects. The bulk of this plasticizer renders it permanent in the film and at the same time increases its tensile strength; this contributes to rigidity, particularly noticeable at low temperatures.

## ACKNOWLEDGMENT

A number of the determinations, particularly those of resistance characteristics of the films, were made by Michael Kouris.

The determinations of tensile strength were carried out in the Department of Chemistry of the Ontario Research Foundation, Toronto, Ontario.

## REFERENCES

- (1) Aiken, W., Alfrey, T., Janssen, A., Mark, H., J. Polymer Sci. **2**, 178, (1947).
- (2) American Society for Testing Materials, Philadelphia, Pa., Method D882-49T.
- (3) Ibid., Method D1043-51.
- (4) Buttrey, D. C., "Plasticizers," Cleaver-Hume Press, Ltd., 1950.
- (5) Clash, R. F., Jr., Berg, R. M., Ind. Eng. Chem. **34**, 1218 (1942).
- (6) Doolittle, A. K., "The Technology of Solvents and Plasticizers," Chap. 15, Wiley, New York, 1954.
- (7) Lawrence, R. R., McIntyre, E. B., Ind. Eng. Chem. **41**, 689 (1949).
- (8) Petzold, O., Chemical Supply Co., Ltd., Tech. Service Memo. **57**, July 1945.
- (9) Reed, M. C., Harding, J., Ind. Eng. Chem. **41**, 675 (1949).
- (10) U. S. Industrial Chemicals, Inc., Chem. Eng. News **33**, 2242 (1955).

Received for review January 14, 1956 Accepted April 19, 1956