

## Cardanol Derivatives as PVC Plasticizers. II. Plasticizer Evaluation

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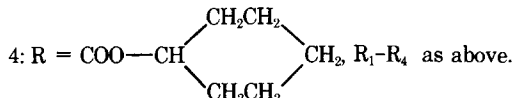
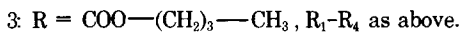
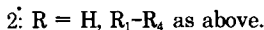
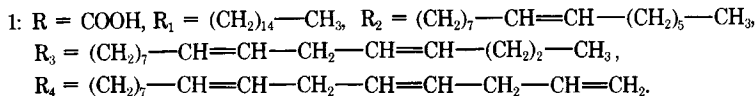
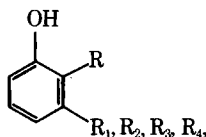
### Synopsis

A series of cardanol derivatives prepared in a preceding study<sup>1</sup> are evaluated as PVC plasticizers. These include butyl anacardate (3), cyclohexyl anacardate (4), 3-(pentadec-8'-enyl)phenyl acetate (5), 3-(8',9'-diacetoxypentadecyl)phenyl acetate (6), and 3-(8'-epoxypentadecyl)phenyl acetate (7). The evaluation initially involves compatibility and Brabender plastification testing. The two acetates 6 and 7 as the most promising compounds are selected for further investigation, comprising the determination of tensile properties and thermal stability behavior of compression-molded plasticized PVC sheet material. The extrudability of a plasticized wire coating formulation is also studied. The plasticizing efficiency of both 6 and 7 is on a par with di(2-ethylhexyl) phthalate used as a standard plasticizer. In addition, both acetates show distinct costabilizing efficiency, the epoxyacetate 7 in this respect being superior to the other compounds tested. Cardanol, readily available as a by-product of cashew nut processing, thus may represent a welcome addition to the strained raw material market in the plasticizer field.

### INTRODUCTION

Cashew-nut-shell liquid (CNSL), a commercially important by-product of cashew-nut processing, has been the topic of considerable research activity in both the purely scientific and the applied fields. The principal ingredient, constituting some 90% of the liquid, is anacardic acid,<sup>2</sup> a mixture of salicyclic acid derivatives possessing C<sub>15</sub> hydrocarbon side chains of variable unsaturation as represented by 1. Another, though minor CNSL constituent is cardanol, 2, a mixture of related phenols lacking the carboxylic function.<sup>3</sup> In the commercial cashew nut roasting process, 2 arises from 1 by decarboxylation. The commercial distillation of CNSL, therefore, leads to a product essentially composed of cardanol, which, depending on the thermal history of the shell liquid in the course of both nut processing and distillation, contains the mono-, di-, and triolefinic phenol congeners in considerably varying proportions. While a product obtained under reasonably mild processing conditions generally possesses a high extent of unsaturation typically corresponding to almost two olefinic double bonds per average molecule, an excessively heat-treated cardanol has lost much of its unsaturated character through selective thermal polymerization of the higher unsaturated olefins and may thus well show unsaturation equivalent to little more than one double bond per average molecule.<sup>4</sup>

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CNSL, as well as cardanol itself and some of its derivatives, have over the years found rewarding industrial outlets, notably in the technology of polymeric resins for coating and adhesive applications and in the manufacture of grinding wheel and brake lining materials. These topics have recently been reviewed by Aggarwal<sup>5</sup> and Welgemoed.<sup>6</sup>

With our interest focused on the potential use of cardanol derivatives in the plasticization of poly(vinyl chloride) (PVC), we recently<sup>1</sup> prepared a number of compounds possessing the cardanol molecular skeleton for an evaluation of their plasticizing efficiency. This evaluation study is described in the present account.

## RESULTS AND DISCUSSION

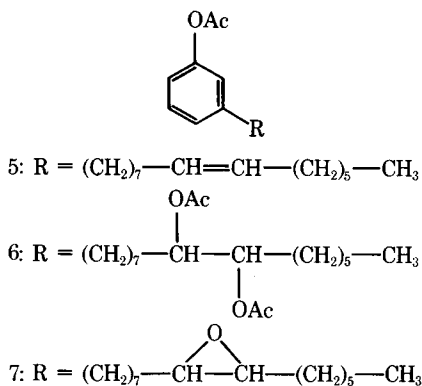
The plasticizing efficiency of an additive depends, among other factors, on the presence of suitable polar, polarizable, and nonpolar groups in the molecule.<sup>7-10</sup> Compounds of entirely polar character are unsuitable as plasticizers, and so are compounds with an exclusively nonpolar structure. In either case, the additive's molecules associate with each other rather than with polymer segments and migrate to the surface to form an oily or tacky film. The presence of both polar and nonpolar structural entities in an additive is a minimum requirement of plasticizing behavior. In a plasticizer of this type, exemplified by the adipates or sebacates of 2-ethylhexanol and related alkanols, the ester function as the polar part attaches to a dipole in the polymer, whereas the hydrocarbon groups as the nonpolar portions increase the interchain distances in the polymer bulk and prevent other polymer dipoles from mutual electrostatic interaction, thus acting as shielding barriers between polymer segments. The effect of plasticization with compounds of this type (designated by Leuchs<sup>10</sup> as "shielding" plasticizers) is essentially one of lowering the polymer's glass transition temperature and improving the flexibility at low temperatures, although the price to be paid for this benefit is an increase in the gelling temperature (signifying poorer gelling behavior) and generally a reduced measure of compatibility with the polymer base.

In a second type of plasticizer, represented by di(2-ethylhexyl) phthalate, dinonyl phthalate, and other aromatic esters, a polarizable group constitutes an additional part of the molecule. The presence of such a polarizable entity

introduces a hinging effect into the polymer-plasticizer aggregate, as now the polar (ester) and the polarizable (aromatic) groups each may attach to a different polymer dipole, thus connecting the two dipoles via a flexible bridging system in the plasticizer. Representatives of this class of additives, hence, are aptly named "hinging" plasticizers.<sup>10</sup> Generally, enhanced compatibility and improved gelling characteristics (although less pronounced cold flexibility) relative to the first-named plasticizer type are the result of such interplay between both polar and polarizable entities in the compound. It has been recognized that optimal plasticizing efficiency is attained only when the intermolecular bonding forces within the additive arising from these various structural entities are comparable in magnitude with both the secondary bonding forces operative between plasticizer and polymer and the interchain attractive forces within the polymer itself.

The following compounds, previously prepared,<sup>1</sup> were selected for the present plasticizer evaluation study: *n*-butyl anacardate (3), cyclohexyl anacardate (4), 3-(pentadec-8'-enyl)phenyl acetate (5), 3-(8',9'-diacetoxypentadecyl)phenyl acetate (6), and 3-(8'-epoxypentadecyl)phenyl acetate (7).

In addition to nonpolar aliphatic chains or chain segments, these structures all comprise ester groups and benzene rings comparable in polarity and polarizability with the common phthalates. Compounds 5-7, therefore, should exhibit the gelling and plasticizing behavior characteristic of these hinging-type plasticizers:



The anacardates 3 and 4 both, in addition, possess a phenolic hydroxyl function the polarity of which is generally too high to provide adequate PVC compatibility. Although some diminution in compatibility would, therefore, have to be accepted,\* we decided to include the two anacardates in the present evaluation as we were primarily interested in an assessment of the antioxidant effects that could be anticipated to arise from the unprotected phenolic system.<sup>11,12</sup> A somewhat reduced compatibility might also be expected with the monoacetate 5 for lack of an additional polar site within the long hydrocarbon side chain. Aromatic esters with alkyl groups larger than C<sub>12</sub> generally are unsuitable as primary plasticizers because of excessive paraffinic character. It was, moreover, realized that the olefinic unsaturation in the side chains of 5, contributing to

\* Both cardanol and anacardic acid, lacking the additional ester group present in 3 and 4, could be expected to be even less compatible, and indeed the extent of incompatibility observed in a preliminary examination was such that neither product was employed in subsequent investigations.

TABLE I  
PVC Test Formulation

Component	Content, parts by weight
PVC resin <sup>a</sup>	57
Plasticizer	40
Stabilizer <sup>b</sup>	2
Lubricant <sup>c</sup>	1

<sup>a</sup> Corvic D 65/6<sup>b</sup> Interstab M 103 ZF<sup>c</sup> Loxiol G13

instability in oxidative and UV-radiative environments, would diminish the compound's effectiveness in a PVC blend. On the other hand, the efficacious lubricating properties of long-chain aliphatic esters are well known,<sup>13,14</sup> and we wished to investigate 5 as a plasticizer with additional processing aid characteristics. The acetate 7 was included in this study for reasons of expected costabilizing effects exerted by the oxiran ring system as in the common epoxy plasticizers.

### Preliminary Screening

In a preliminary small-scale compatibility testing program, a series of 10-g PVC batches of the general formulation given in Table I were made up in which the plasticizer component was varied from 3 through 7. A "blank" formulation containing di(2-ethylhexyl) phthalate (DIOP) as standard plasticizer was included for comparison. The poly(vinyl chloride) resin used was a suspension grade of medium *K* value (corvic D 65/6); the formulations were stabilized with a barium-cadmium soap (Interstab M 103 ZF, formerly Advastab BC 103 ZF) and were lubricated with a glycerol fatty acid ester (Loxiol G13). The PVC compounds were compression molded at 160°C into flat plate specimens each with dimensions 20 × 30 × 3 mm. The plates were inspected visually. The blank plate containing DIOP, off-white in color and translucent, was flexible and dry in surface appearance, and as expected showed complete plasticizer compatibility. Both the triacetate 6 and the epoxyacetate 7 gave flexible specimens of the same surface appearance, albeit slightly yellow in color, and exhibited the same complete compatibility. No changes in these respects were noticed in the three plates after two months of storage at room temperature. The anacardates 3 and 4, on the other hand, were compatible only to a limited extent and showed a tendency to "sweat out." Accordingly, the yellowish specimens were strongly opaque and, although still flexible, exposed an exudate on the surface which, after several days, formed a thick, oily film. An intermediate behavior was observed with the specimen derived from the monoacetate 5; the yellowish plate, while of dry surface appearance, was slightly stiffer and less transparent than the DIOP specimen.

Although both 3 and 4 in combination (equal parts) with DIOP proved considerably more compatible with the polymer base, the expected antioxidant effects, monitored in a comparative milling test at 170°C in an impinging stream of compressed air, were not sufficiently ostentatious relative to a DIOP formulation to warrant further evaluation.

TABLE II  
Brabender Test Results

Plasticizer <sup>a</sup>	$\tau_{10}$ <sup>b</sup>	$\tau_{\max}$ <sup>b</sup>	$t_{\max}$ , <sup>c</sup> min
DIOP	245	455	1.0
5	92	96	6.2
6	230	590	0.6
7	205	495	0.6

<sup>a</sup> In test formulation as per Table I.

<sup>b</sup> Torque values after 10 min and at maximum, respectively; arbitrary units.

<sup>c</sup> Time to reach  $\tau_{\max}$ .

### Brabender Testing

The subsequent testing program, involving compounds 5–7 and, again, DIOP as a standard, was conducted in a Brabender Plastograph operated at 132°C. This instrument allows measurement of the torque exerted by the mixing propellers as the PVC blend is compounded. The torque measured after a reasonable mixing period (arbitrarily set at 10 min in this work) reflects the amount of energy absorbed in the plasticization process, a high torque value indicating a high degree of gelling. Furthermore, the time elapsed to reach maximum torque is a reliable indicator of the rate of plasticizer absorption (“solution”) by the polymer resin. The two criteria taken together represent a useful measure of a compound’s plasticizing efficiency. The PVC blends employed were of the compositions given in Table I, batch size being limited to 35 g. The results of these Brabender tests are summarized in Table II, which for each formulation lists the torque measured after 10 min of mixing time ( $\tau_{10}$ ), the maximum torque attained ( $\tau_{\max}$ ), and the time required to reach maximum torque ( $t_{\max}$ ). The torque values listed are relative instrument readings and, hence, are given in arbitrary units.

The tabulated findings permit the following conclusions: (i) In relation to the DIOP standard, acetate 5 gives low  $\tau_{10}$  and  $\tau_{\max}$  readings, with  $t_{\max}$  raised sixfold. This indicates good lubricating characteristics, but rather inferior plasticizing efficiency and suggests discontinuation of testing efforts with that compound. (ii) Both 6 and 7, giving  $\tau_{10}$  and  $\tau_{\max}$  values in the neighborhood of those resulting from the standard formulation, compare well with DIOP in their gelling characteristics. The maximum torque in both cases actually exceeds that of the DIOP formulation by some 10–30%, whereas the gelling time is reduced by 40%. Although these figures are not necessarily representative, as the limited quantities of compounds available at this stage did not permit repetitive tests, it appears safe to state that both acetates are at least equivalent to the DIOP standard in their gelling behavior. This finding prompted the synthesis of larger quantities of the two compounds 6 and 7 for the mechanical and stability investigations described in the subsequent two sections.

### Mechanical Testing

Three formulations according to Table I (100-g batches), containing DIOP, 6, and 7, respectively, were mixed in the Brabender Plastograph for 10 min at 132°C. The blends were compression molded at 160°C to flat sheets of 2-mm

thickness. Tensile tests were conducted on specimens cut from the sheets. The results, including tensile strength at break ( $\sigma$ ), elongation at break ( $\epsilon$ ), and modulus of elasticity at 100% elongation ( $E_{100}$ ), are compiled in Table III under the heading "virgin material."

The data show both acetates to be on a par with DIOP in tensile behavior. Compound 6 appears to afford slightly stronger, and 7 slightly weaker, specimens than provided by DIOP, although, again, a larger number of tests will be required to establish any clear trends.

### Thermal Stability Testing

The same three formulations as used for the mechanical tests were employed for thermal stability testing. This involved the following three approaches: (i) mechanical testing after controlled heat aging, (ii) differential thermal analysis (DTA), and (iii) color monitoring during controlled heat aging. The required specimens were cut from the compression-molded sheets obtained under the preceding heading.

In the first approach, two sets of tensile specimens were aged at 190°C in air for 30 and 60 min, respectively. Room-temperature tensile tests were performed on these two sets. The results are listed in Table III. It is immediately apparent from the data that the standard formulation suffers a noticeable loss in tensile strength and elongation, and a concomitant increase in modulus, upon exposure to the elevated temperature; this is especially obvious after the 60-min treatment, at which point  $\sigma$  is reduced by 15%, and  $\epsilon$  by 60%, whereas  $E_{100}$  has increased by 112%. In notable contrast, the formulations incorporating 6 and 7 both give virtually unchanged  $\sigma$  and only moderately reduced (24–36% after 60 min)  $\epsilon$  values, the latter now amounting to almost twice the value measured on the standard; the moduli undergo an increase (after 60 min) by appreciably less than half of that found with DIOP. A clear trend of increasing thermal stability, in terms of strength retention after heat aging, on going from the standard to the two formulations containing 6 and 7 is thus apparent. On comparing 6 with 7, one finds the former slightly superior in this respect.

In the differential thermal analysis approach, bulk samples were subjected to a DTA scan in static air at a heating rate of 8°C/min in a differential thermal

TABLE III  
Tensile Properties<sup>a</sup> of PVC Formulations

Plasticizer <sup>b</sup>	Virgin material			Aged for 30 min at 190°C			Aged for 60 min at 190°C		
	$\sigma$ , <sup>c</sup> MN m <sup>-2</sup>	$\epsilon$ , <sup>d</sup> %	$E_{100}$ , <sup>e</sup> MN m <sup>-2</sup>	$\sigma$ , <sup>c</sup> MN m <sup>-2</sup>	$\epsilon$ , <sup>d</sup> %	$E_{100}$ , <sup>e</sup> MN m <sup>-2</sup>	$\sigma$ , <sup>c</sup> MN m <sup>-2</sup>	$\epsilon$ , <sup>d</sup> %	$E_{100}$ , <sup>e</sup> MN m <sup>-2</sup>
DIOP	14.6	432	3.4	13.5	273	4.9	12.5	174	7.2
6	16.8	445	3.8	17.0	371	4.6	16.6	337	4.9
7	13.5	467	2.9	13.2	365	3.6	13.4	301	4.5

<sup>a</sup> Per Fed. Test Method Std. No. 406, Method 1011, (ASTM D 638); all tests at room temperature. Entries represent averages of five test runs.

<sup>b</sup> Formulations as per Table I.

<sup>c</sup> Tensile strength at break.

<sup>d</sup> Elongation at break.

<sup>e</sup> Modulus of elasticity at 100% elongation.

TABLE IV  
Degradation Temperatures<sup>a</sup> of PVC Formulations  
Determined by Differential Thermal Analysis<sup>b</sup>

Plasticizer <sup>c</sup>	Degradation temp., °C
DIOP	210
6	255
7	283

<sup>a</sup> Temperature of first major exotherm.

<sup>b</sup> In static air; heating rate 8°C/min.

<sup>c</sup> Formulations as per Table I.

analyzer. The degradation temperatures as determined from the recorded major exotherms are given in Table IV. The figures confirm the superior thermal stability of the formulations plasticized with 6 and 7 relative to DIOP, the epoxidized compound in this respect showing the best performance.

The third approach involved an aging test in which discoloration resulting from HCl elimination and oxidation<sup>15</sup> was monitored as a function of aging time at 190°C. To this end, chips of 2 cm<sup>2</sup> surface area (one set of 12 for each formulation) were subjected to a heat treatment at 190°C in air, and at specified periods of time, a specimen was removed from each formulation. The experiment was conducted over a period totaling 300 min. A comparison of the colors shown by the chips revealed the expected steady trend of discoloration ranging from a light brown (fawn) in the early stage to a dark reddish-brown and ultimately to a deep black as the heat treatment proceeded.

Significantly, the samples incorporating 6 and 7 displayed discoloration in the sequence stated after heating periods appreciably longer than observed with the DIOP standard samples. Equivalent color hues and associated heating periods for the three formulations are given in Table V. It is seen that the fawn stage is reached after 40 min by the sample containing 7, after 20 min by that containing 6, and after only 10 min by the standard. More conspicuously yet, the dark reddish-brown stage, reflecting a significant extent of dehydrochlorination, is attained by the standard after 30 min, whereas it takes about 2.5 and 4 hr, respectively, for the samples with 6 and 7 to reach the same stage. Finally, the specimens containing DIOP and 6 blackened entirely after about 1.5 and 3.5 hr, respectively, and the one incorporating 7 was not completely black yet at the end of the experiment (6 hr). The epoxyacetate 7, conforming to expectation,

TABLE V  
Discoloration of PVC Formulations During Heat Aging Test<sup>a</sup>

Plasticizer <sup>b</sup>	Time period required to reach color stage, min			
	Light brown	Light reddish-brown	Dark reddish-brown	Black
DIOP	10	25	30	90
6	20	80	160	220
7	40	140	250	≥ 300 <sup>c</sup>

<sup>a</sup> Aging test performed at 190°C in air.

<sup>b</sup> Formulations as per Table I.

<sup>c</sup> Sample not completely black after 300 min.

TABLE VI  
PVC Wire-Coating Formulation

Component	Content, parts by weight
PVC resin <sup>a</sup>	67
Triacetate 6	28
Stabilizer <sup>b</sup>	4
Lubricant <sup>c</sup>	0.7

<sup>a</sup> Corvic D60/11.

<sup>b</sup> Tribasic lead sulfate.

<sup>c</sup> Spicco CA 103 (calcium stearate).

thus performs best among the three formulations tested, showing a synergistic stabilizing efficiency some 50% higher than demonstrated by the triacetate 6. (It is of interest to compare these results with an earlier study<sup>16</sup> in which the Ba/Cd epoxy combination showed only minor synergism in PVC stabilization. The epoxy plasticizer used in that work, an epoxidized soybean oil, is devoid of the phenyl acetate moiety present in 7, which may thus be implicated as a structural system responsible for some of the synergistic characteristics shown by the cardanol compound.)

On balance, and taking the results of all three types of thermal tests into account, one finds that both acetates are distinctly superior to DIOP in heat stability and strength retention after short-term thermal aging at the high test temperature employed.

### Extrusion of Wire-Coating Formulation

An 800-g batch of a typical unpigmented wire-coating PVC formulation plasticized with acetate 6 according to Table VI was granulated and extruded in an effort to establish the behavior of a selected cardanol-type plasticizer under conditions of wire coating and cable sheathing extrusion. A corresponding batch plasticized with DIOP was subsequently extruded on the same machine at identical extruder settings. The extrudate, a continuous tubular profile with nominal 2 mm I.D. and 4 mm O.D., in both cases showed smooth inner and outer

TABLE VII  
Tensile Properties<sup>a</sup> of Extruded PVC Wire-Coating Blend

Plasticizer <sup>b</sup>	Tested 48 hr after extrusion <sup>c</sup>		Tested 1 yr after extrusion <sup>d</sup>	
	$\sigma$ , <sup>e</sup> MN m <sup>-2</sup>	$\epsilon$ , <sup>f</sup> %	$\sigma$ , <sup>e</sup> MN m <sup>-2</sup>	$\epsilon$ , <sup>f</sup> %
DIOP	20.7	384	21.3	273
6	25.0	438	25.4	313

<sup>a</sup> Per Fed. Test Method Std. No. 406, Method 1011 (ASTM D638), except that specimens were used as cut from extrudate. Entries represent averages of five test runs.

<sup>b</sup> Formulation as per Table VI (same for standard, except with DIOP in lieu of 6).

<sup>c</sup> Conditioned at 23° ± 1°C, 50 ± 4% R.H.

<sup>d</sup> Stored at 20° ± 8°C, 55 ± 20% R.H., and conditioned for 48 hr as in (c), prior to testing.

<sup>e</sup> Tensile strength at break.

<sup>f</sup> Elongation at break.



surfaces. The test material was cream colored, whereas the standard was grayish-white. Tensile properties, determined on the extruded materials immediately and again after one year of storage, are listed in Table VII.

The data show the test formulation to be superior to the standard in both  $\sigma$  and  $\epsilon$ , although the differences (10–20%) are by no means significant. The long-term stored samples show an ever so slight increase in  $\sigma$ , while a moderate (29%) reduction in  $\epsilon$  is apparent for both formulations.

### Conclusions

The test program discussed reveals a most promising performance of the cardanol derivatives 6 and 7 as PVC plasticizers. In comparison to DIOP as the standard, both compounds incorporated into PVC formulations, while tending to impart a slight yellowish discoloration, exhibit superior plasticizing efficiency and, upon short-term heat treatment at 190°C, show better strength retention, paired with less embrittlement, and higher resistance to degradation. The high-temperature performance indicates costabilizing, and possibly synergistic, effects to be exerted by the two cardanol derivatives, notably the epoxide 7. We must emphasize, however, that the findings here presented are preliminary, and considerably more testing work, including the determination of cold flex properties, electrical, volatility, and migration behavior, water and solvent resistance, milling and injection-molding characteristics, and long-term aging at moderately elevated temperatures (80–100°C), will be required for an adequate plasticizer characterization. It is, furthermore, of interest to study other modifications of the cardanol structure, such as represented by the epoxidized anisole analog of 7 or higher alkanolic ester analogs of 6, which can be expected to possess superior hydrolytic stability. It is intended to include these features in future investigations.

### EXPERIMENTAL

**PVC Resin.** The PVC types, Corvic D65/6 and D60/11, both suspension grades, were commercial resins (African Explosives and Chemical Industries, Ltd.) with Fikentscher *K* values of about 70 and 65, respectively.

**Plasticizers and Other Additives.** The anacardates 3 and 4, as well as the acetates 5–7, were obtained in the preceding work.<sup>1</sup> Larger quantities required for Brabender and extrusion testing were synthesized by the known<sup>1</sup> procedures. Di(2-ethylhexyl) phthalate (DIOP) was a commercial product, as were the stabilizers and lubricants used per Tables I and VI.

**Small-Scale Compatibility Testing.** The general formulation of Table I was employed throughout. The liquid additives (plasticizer, 4.0 g; stabilizer, 0.2 g; lubricant, 0.1 g) were mixed and subsequently homogenized with the PVC resin (5.7 g). Batches so prepared with each of the plasticizers 3–7, as well as with DIOP standard, were compression molded at 160°C in a Carver hydraulic press (cavity dimensions 20 × 30 × 3 mm; platens preheated to 160°C; mold closed at contact pressure) for 5 min at 0.16 MN m<sup>-2</sup>. Mold and platens were cooled to a room temperature (pressure increased to 0.24 MN m<sup>-2</sup> during cool-down period) before the specimens were removed. After storing for 48 hr under standard conditions (23° ± 1°C, 50 ± 4% relative humidity), the samples were visually examined as described in the text.

**Brabender Testing.** Four 35-g batches, incorporating DIOP and compounds 5–7 as plasticizers and formulated as per Table I, were prepared and homogenized as in the small-scale tests except that 3.5-fold quantities of resin and additives were used. The Brabender Plastograph, preheated to 132°C, was charged with a batch, and mixing was started. Both the maximum torque ( $\tau_{\max}$ ) and the torque after 10 min of mixing time at the given temperature ( $\tau_{10}$ ) were recorded as arbitrary instrumental readings, and the time ( $t_{\max}$ ) to reach  $\tau_{\max}$  was taken. The data are shown in Table II.

**Mechanical Testing.** Three 100-g batches, incorporating DIOP and compounds 6 and 7 as plasticizers and formulated as per Table I, were prepared and homogenized as in the preceding tests and were partially gelled by Brabender mixing for 10 min at 132°C. The batches were compression molded to flat sheets of 2-mm thickness in the Carver press under the conditions used in the small-scale compatibility testing. Tensile specimens per Federal Test Method Standard No. 406, Method 1011, Type I, were cut from the sheets. The specimens (set of five for each one of the three formulations) were subjected to tensile tests per cited test method on an Instron testing machine. Tensile strength at break ( $\sigma$ ), elongation at break ( $\epsilon$ ), and modulus of elasticity at 100% elongation ( $E_{100}$ ) were evaluated from the stress–strain curves recorded. The data were averaged over the five runs of each set.

Two more sets, each of five tensile specimens, for each of the three formulations were placed into a circulating-air oven preheated to 190°C and were maintained at that temperature for 30 and 60 min, respectively. Values of  $\sigma$ ,  $\epsilon$ , and  $E_{100}$  for the three sets removed after 30 min, as well as for the three corresponding sets removed after 60 min, were taken from the stress–strain curves recorded at room temperature as before and were averaged over the five runs of each set. The averages for both the virgin and the heat-treated samples are compiled in Table III under the proper headings.

**Differential Thermal Analysis.** An Aminco Thermo Analyzer equipped with platinum/platinum–rhodium thermocouples was employed for the DTA tests conducted over the 25°–400°C temperature range at a heating rate of 8°C/min in static air. The samples used were chips of about 20 mg weight cut from the compression-molded sheets prepared for the mechanical testing. The temperature readings taken from the major exotherm maxima of the thermograms are given as degradation temperatures in Table IV.

**Discoloration Tests at 190°C.** Rectangular chips of approx. 2 cm<sup>2</sup> surface area, a total of 12 for each one of the three formulations, were cut from the compression-molded sheets prepared for the mechanical testing. The specimens were placed into a forced-draft oven preheated to 190°C and were removed, one at a time from each formulation, after intervals ranging from 10 min initially to 40 min near the end of the experiment. Discoloration of the chips was assessed visually. The periods of heat aging required for the different formulations to reach four arbitrarily selected color thresholds are recorded in Table V.

**Extrusion of Wire-Coating Formulation.** A batch consisting of PVC resin (556 g), plasticizer 6 (235 g), stabilizer (33.4 g), and lubricant (5.56 g) according to the formulation of Table VI was thoroughly mixed by hand and was gelled for 12 min on a Bridge laboratory mill at roller temperatures of 140°C (back) and 150°C (front) and a friction ratio of 1:1.15. Disintegration of the gelled and cooled material in a random granulator was followed by extrusion on a single-

screw Berstorff extruder (30-mm screw diameter) operated at 50 rpm, head temperature 165°C. A tubular die was employed that permitted extrusion to a hollow round profile with nominal 2-mm I.D., 4-mm O.D. (periodic dimensional checks on the cooled profile revealed an actual wall thickness of  $0.85 \pm 0.03$  mm). A batch identical in all aspects except that it contained DIOP in place of 6 was extruded on the same machine under identical conditions immediately following the first batch, the intermediate charge being marked with a red pigment. Having passed through a room-temperature water bath, the extrudate was collected without tension on a takeup reel and was stored for 48 hr under standard conditions. Samples 10 cm long taken at random from the extrudate (five specimens for each formulation) were checked for dimensions (wall thickness, cross-sectional area) and were subjected to tensile tests on an Instron testing machine. The values of  $\sigma$  and  $\epsilon$ , averaged over the five runs per formulation, are given in Table VII. The same tests were performed on a portion of the material stored for one year under roof ( $20^\circ \pm 8^\circ\text{C}$ ,  $55 \pm 20\%$  R.H.). The results are listed in the same table.

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