consumption leads to a transition stage which is directly responsible for the viscosity increase; a constant peroxide consumption would result, therefore, in a constant rate of viscosity increase for all reactions carried out in the specified temperature range. This is in accordance with the results presented in Figure 3. Experimental observations indicate that at a later stage of the reaction the ratio of the concentration of peroxides formed to the concentration consumed changes; greater quantities of peroxides at equivalent viscosities are present in the oil as the reaction temperature is lowered. This could well be due to different peroxide stabilities occasioned perhaps by different reactivities of the peroxides formed from the mono and polyunsaturated fatty acid segments of the triglyceride.

For any given oil the maximum peroxide value is an inverse function of temperature; at lower temperatures higher values are obtainable. Accordingly it is indicated that the rearrangement to the transition stage becomes slower at the lower temperatures and the change in the viscosity rate curve should occur at lower viscosities with lowering of the temperature. For these reasons, it must be assumed that peroxide consumption at the later stages of oxidation only is dependent on the temperature of the reaction.

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Oxaglycol Esters as Polyvinyl Chloride Plasticizers

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Twenty-seven esters of diethylene glycol, triethylene glycol, and similar oxaglycols have been prepared and tested as plasticizers for polyvinyl chloride. Aliphatic and mixed aliphatic-aromatic esters showed good compatibility and low volatility and imparted excellent low temperature flexibility. The purely aromatic esters were generally compatible and less volatile but exhibited poorer low temperature flexibility. All the compositions ranged from fair to excellent in heat stability.

THE use of aliphatic esters of diethylene glycol and triethylene glycol as plasticizers is well known. However, except for a report (*4, 5*) that diethylene glycol dibenzoate was used as a polyvinyl chloride plasticizer in Germany, aromatic esters of this type have received little attention. It therefore seemed of interest to prepare aromatic and mixed aliphatic-aromatic esters of diethylene glycol and triethylene glycol. A mixed aliphatic-aromatic ester of ethylene glycol, the acetate-benzoate, was described recently after this work had been completed (*3*).

The study of glycol esters also has been extended to esters of thiodiglycol and to esters of glycols containing a higher percentage of carbon, including those obtained by treating tetramethylene glycol and pentamethylene glycol with ethylene oxide. Two esters of 5-oxa-1,9-nonanediol also have been included. Mixed aliphatic esters of this glycol were made in Germany (*6*).

RAW MATERIALS

The diethylene glycol, triethylene glycol, and thiodiglycol were standard products of the Carbide and Carbon Chemicals Corporation. Tetramethylene glycol and pentamethylene glycol were obtained from E. I. du Pont de Nemours & Company. Bis-(4-chlorobutyl)ether was prepared by treating tetrahydrofuran from the Celanese Corporation with thionyl chloride in the presence of concentrated sulfuric acid (*7*). The product, obtained

Table I. Esters

Ester	Time, Hours	Temp., ° C.	% Conv.[a]	Boiling Point ° C.	Boiling Point Mm.	n_D^{25}
Diethylene glycol						
Dibenzoate	40	180–220	60	180–184	0.3	1.5435
Benzoate-caprate	26	200–220	86	172–192	0.2	1.4868
Benzoate-caprylate	16	210–220	90	167–179	0.25	1.4880
Benzoate-levulinate	6.5	200	66	185–190	0.3	1.4990
Benzoate-oleate (2.5:1)[b]	16	210–235	73	...	...	1.4980
Benzoate-oleate (5:1)[b]	20	210–230	80	...	...	1.5150
Benzoate-pelargonate	20	200–220	54	166–183	0.3	1.4825
Caprate-toluate	21	180–200	63	180–195	0.2	1.4787
Bis-*m*-chlorobenzoate	19	200–220	56	196–205	0.2	1.5560
o- and *p*-chlorobenzoate (2:1)[b]	27	160–170	70	...	...	1.5560
Laurate-*m*-toluate	8.5	185–210	65	195–212	0.25	1.4830
Ditoluate	16	190–200	78	196–200	0.3	1.5402
Triethylene glycol						
Benzoate-caprylate	19	195–210	78	185–204	0.25	1.4818
o- and *p*-chlorobenzoate (2:1)[b]	25	165–180	45	...	...	1.5466
Ditoluate	19	190–200	45	224–235	0.5	1.5320
3-Oxa-1,7-heptanediol						
Dibenzoate	22	170–190	45	207–212	0.4	1.5341
Dicaprylate[c]	1	160–185	81	184–188	0.3	1.4440
Bis-2-ethylhexoate	22	170–190	32	174	0.4	1.4414
Dilevulinate	16	170	81	201–209	0.4	1.4562
Di-*p*-toluate[c]	24	170	65	213–225	0.3	1.5325
3-Oxa-1,8-octanediol						
Bis-2-ethylhexoate	20	205–230	48	188–191	1.0	1.4425
Ditoluate	64	160–200	63	205–220	0.2	1.5310
5-Oxa-1,9-nonanediol						
Dibenzoate	..	...	54	200–215	0.2	1.5266
Dicaprylate	..	...	58	217–221	0.6	1.4453
Dioxa-1,10-decanediol						
Dicaprylate	18	180–200	55	190–192	0.2	1.4460
3-Oxa-1,8-octanediol + dioxa-1,11-undecanediol (b.p. 145–195°/11 mm.)						
Bis-2-ethylhexoate[c]	..	...	75	180–200	0.7–0.4	1.4430
Thiodiglycol						
Dibenzoate	29	170–190	64	200–203	0.3	1.5686
Benzoate-caprylate	18	200	82	190–204	0.3	1.5116
Benzoate-2-ethylhexoate	16	195–200	70	165–195	0.25	1.5056

[a] In mixed esters conversion is computed on basis of equimolar mixture.
[b] Mole ratio as charged.
[c] 0.1 to 0.3% *p*-toluenesulfonic acid added as catalyst.

in 50% conversion, boiled at 132–136° at 20 mm. (84–86° at 0.5 mm.) (*1*), n_D^{25} 1.4554 (n_D^{25} 1.4567) (*1*). The mixture of toluic acids was obtained by oxidizing nitration grade coal tar xylene. The capric acid was obtained from Lever Brothers Company and the pelargonic acid was supplied by Emery Industries, Inc.

OXAGLYCOLS

Ethylene oxide was passed into 360 grams of 1,4-butanediol held at 100° C. and containing 3.6 grams of potassium hydroxide until 197 grams of the gas had been absorbed. The cooled, black product was treated with 10 ml. of water and an excess of carbon dioxide. On fractionation through a helices-packed 52 × 2 cm. column the following cuts were obtained: 107 grams of 1,4-butanediol, boiling point 131–142° at 20 mm.; 21 grams of intermediate, boiling point 142–158° at 20 mm.; 152 grams (40% yield) of 3-oxa-1,7-heptanediol, boiling point 156–157° at 18 mm.; 26 grams of a second intermediate, boiling point 157–186° at 18 mm.; and 127 grams (25% yield) of mixed dioxa-1,10-decanediols, boiling point 185–190° at 17 mm. (decomposed), n_D^{25} 1.4546. There was a 110-gram residue. Pure 3-oxa-1,7-heptanediol boiled at 158° at 16 mm., n_D^{25} 1.4518. The above dioxa-1,10-decanediol fraction was redistilled to give 93 grams of purer material, boiling point 186–191° at 19 mm., n_D^{25} 1.4552.

In the same manner 71 grams of ethylene oxide were added to 500 grams of 1,5-pentanediol in the presence of 5 grams of sodium hydroxide. Fractionation of the neutralized product yielded: 305 grams of 1,5-pentanediol, boiling point 140–144° at 20 mm.; 85 grams of intermediate, boiling point 144–167° at 20 mm.; and 93 grams (33% yield) of 3-oxa-1,8-octanediol, boiling point 167° at 20 mm., n_D^{25} 1.4544–1.4538. Pure 3-oxa-1,8-octanediol boiled at 167° at 20 mm., n_D^{25} 1.4544. The 65-gram residue from the original distillation was fractionated to yield 23 grams of a second intermediate, boiling point 167° at 20 mm. to 142° at 0.5 mm., and then 21 grams (6% yield) of mixed dioxa-1,11-undecanediols, boiling point 142–146° at 0.5 mm., n_D^{25} 1.4567.

Analytical data for these oxaglycols are included in Table II.

ESTERS

A mixture of 220 grams of caprylic acid, 40 ml. of toluene, and 30 grams of sodium hydroxide was refluxed for 16 hours while the evolved water was collected in a Dean and Stark trap. After the addition of 50 grams of bis-(4-chlorobutyl)ether the mixture was stirred at 165° to 170° C. for 4 hours and then heated for a few minutes at 185°. After cooling, the solution was diluted with 300 ml. of benzene, washed with dilute sodium hydroxide, and distilled. After a 24-gram forerun was separated, there were obtained 60 grams (58%) of 5-oxa-1,9-nonanediol dicaprylate, boiling point 217–221° at 0.6 mm., n_D^{25} 1.4453.

5-Oxa-1,9-nonanediol dibenzoate was prepared in the same way in 54% yield, using ethylene glycol as the reaction solvent. The crude ester distilled at 200–215° at 0.2 mm., n_D^{25} 1.5266. The analytical sample was crystallized from benzene-hexane, melting point 47–48°.

The remaining esters and mixed esters listed in Table I were prepared by refluxing 0.5 mole of the glycol with 1.1 moles of the acid (or 1.1 moles of the mixed acids in 1 to 1 molar ratio unless otherwise indicated) in benzene or toluene solution while the evolved water was collected in a Dean and Stark trap. In some cases 0.1 to 0.3% of *p*-toluenesulfonic acid was added as a catalyst. The reaction product was cooled, diluted with benzene, washed with 10% aqueous sodium hydroxide, and distilled through a 2.5 × 30 cm. Vigreux column. Diethylene glycol *o*- and *p*-chlorobenzoate and triethylene glycol *o*- and *p*-chlorobenzoate were not distilled. The reaction mixtures, after washing, were distilled to a pot temperature of 210° at 0.5 mm. and then the residues were heated and stirred with Attapulgus clay for purification. The first benzoate-oleate (2.5 to 1) was distilled to a pot temperature of 182° at 0.3 mm. and the residue was treated successively with 5 grams of Darco S-51, 10 grams of potassium carbonate, and 10 grams of Attapulgus clay. The second benzoate-oleate (5 to 1) was distilled to a pot temperature of 175° at 0.3 mm. and then treated with 10 grams of Attapulgus clay. The thiodiglycol dibenzoate melted at 63–65° (the Germans reported it to be a solid) (*4*).

ANALYTICAL DATA

Table II summarizes the analytical data for the new, pure compounds prepared and for the mixed chlorobenzoates. In the case of the other mixed esters elemental analyses have no meaning.

PLASTICIZATION TESTS

Plastic sheets were prepared from 60% resin (Geon 101) and 40% of the ester being examined. The plasticizer and resin were dry-blended by mixing at room temperature and this mixture was compounded by milling on a small Thropp roll mill for 5 minutes at 160° C. Sheets of 0.04-inch thickness were molded under a pressure of 2000 pounds per square inch applied for 5 minutes at 160° C. The molded samples were cooled to room temperature

Table II. New Compounds and Mixed Chlorobenzoates

Compound	d_{25}^{25}	Calcd. C	Calcd. H	Found C	Found H
3-Oxa-1,7-heptanediol	1.051	53.8	10.5	53.8	10.9
Dioxa-1,10-decanediols	1.066	54.0	10.1	53.8	10.1
3-Oxa-1,8-octanediol	1.027	56.7	10.8	55.8	11.3
Dioxa-1,11-undecanediols	1.042	56.3	10.4	56.3	10.9
Diethylene glycol bis-*m*-chlorobenzoate	1.307	56.4	4.2	56.6	4.0
Diethylene glycol *o*- and *p*-chlorozoate	1.310	56.4	4.2	56.4	4.5
Triethylene glycol *o*- and *p*-chlorobenzoate	1.287	56.3	4.7	55.0	4.8
3-Oxa-1,7-heptanediol dibenzoate	1.139	70.2	6.4	69.6	7.3
3-Oxa-1,7-heptanediol dicaprylate	0.944	68.4	10.9	68.6	10.8
3-Oxa-1,7-heptanediol bis-2-ethylhexoate	0.942	68.4	10.9	68.4	10.7
3-Oxa-1,7-heptanediol dilevulinate	1.105	58.2	7.9	58.5	7.7
3-Oxa-1,7-heptanediol di-*p*-toluate	1.108	71.3	7.0	71.5	7.1
3-Oxa-1,8-octanediol bis-2-ethylhexoate	0.938	69.0	11.0	68.7	10.3
3-Oxa-1,8-octanediol ditoluate	1.097	71.8	7.3	72.0	7.2
5-Oxa-1,9-nonanediol dibenzoate	M.p. 47–48°	71.3	7.0	71.4	6.9
5-Oxa-1,9-nonanediol dicaprylate	0.937	69.5	11.1	69.6	10.7
Dioxa-1,10-decanediol dicaprylate	0.960	67.0	10.7	66.6	10.7

under pressure, then conditioned for a minimum period of 24 hours at 25° C. and 50% relative humidity. The sheets thus conditioned were the source of the various test specimens.

The esters were designated as incompatible if they failed to flux the resin and form a homogeneous mass on the roll mill, or if they exuded or separated to the surface of the plastic sheet within 30 days of preparation. Borderline compatibility was indicated by a cloudy or hazy sheet without actual visible exudation. A clear sheet was interpreted as indicating complete compatibility.

Heat stability was determined by heating the composition in a compression mold for 30 minutes at 160° C. under molding pressure and observing the color of the resultant sheet. Comparison was made with commercial dioctyl phthalate (fair-good). A plasticizer which was rated as fair did not impart as much heat stability and one rated as good compared favorably with the best commercial dioctyl phthalate.

Low temperature flexibility was measured according to the method of Clash and Berg (*2*). Volatility was measured by heating a weighed, standard-size specimen in a Freas air circulation oven at 105° C. for 24 hours with an air flow of 175 cubic feet per minute across the shelves. Results were expressed as per cent plasticizer lost.

The Shore durometer hardness type A instrument was used to determine the hardness of the plastic compositions. A double 40-mil sheet was placed on the platform directly under the needle of the instrument and the needle lowered down tightly on the sample. Applied pressure was removed and after the lapse of exactly 10 seconds the dial reading was taken. At least three determinations were made on each composition and the average of these results was taken as the final value.

DISCUSSION

Many of the plasticizers tested compared favorably with the better plasticizers currently used by the industry for polyvinyl chloride, when judged on the basis of efficient softening and flexibilizing characteristics, resistance to discoloration from heat, and low rate of evaporation. The purely aliphatic esters were highly flexibilizing but somewhat more volatile than the other esters tested. They seemed to possess borderline compatibility as indicated by the cloudiness of the plasticized sheets. The relatively high water solubility of 3-oxa-1,7-heptanediol dilevulinate diminishes its value as a plasticizer for some applications.

The mixed aliphatic-aromatic esters displayed a favorable balance of properties. Transparency and volatility were generally improved over those given by the straight aliphatic esters, and although some sacrifice was made in flexibilizing efficiency, these esters were satisfactory on this property also. In the case of diethylene glycol benzoate-oleate it was necessary to use a 5 to 1 benzoate-oleate ratio to achieve compatibility. Diethylene glycol laurate-*m*-toluate exuded shortly after making a molded sheet; increase in the benzoate ratio is indicated here as a means of enhancing compatibility.

The aromatic esters imparted only fair flexibility but usually showed appreciably lower volatility than the aliphatic esters. In addition, the chlorinated esters were inferior in softening efficiency. Thiodiglycol dibenzoate and 5-oxa-1,9-nonanediol dibenzoate were both incompatible; it is probably significant that both these compounds also were solids.

Table III. Esters in Polyvinyl Chloride

Ester	Transparency	T_F, °C.	% Plasticizer Loss	Shore Hardness I[a]	Shore Hardness II[b]	Heat Stability
Dioctyl phthalate	Clear	−36	4.1	73	73	Fair-good
Diethylene glycol						
Dibenzoate	Clear	−19	2.4	77	75	Fair
Benzoate-caprate	Clear	−49	2.9	73	69	Good
Benzoate-caprylate	Hazy	−44	7.7	72	72	Very good
Benzoate-oleate (2.5:1)	Incompatible	..	...	..	..	...
Benzoate-oleate (5:1)	Clear	−36	4.3	73	68	Fair
Benzoate-pelargonate	Clear	−50	6.1	70	70	Fair
Caprate-toluate	Clear	−48	4.3	74	70	Good
Bis-*m*-chlorobenzoate	Clear	−11	1.4	80	77	Fair
o- and *p*-chlorobenzoate	Clear	−13	2.1	79	76	Fair
Laurate-*m*-toluate	Hazy	−41	1.3	74	72	Good
Ditoluate	Sl. hazy	−17	2.1	72	72	Good
Triethylene glycol						
Benzoate-caprylate	Cloudy	−47	9.7	70	71	Very good
o- and *p*-chlorobenzoate	Clear	−16	6.8	78	77	Good
Ditoluate	Hazy	−19	7.6	74	71	Good
3-Oxa-1,7-heptanediol						
Dibenzoate	Clear	−23	3.9	72	70	Fair
Dicaprylate	Sl. cloudy	<−60	4.4	69	67	Good
Dilevulinate	Clear	−45	6.7	71	69	Good
Di-*p*-toluate	Clear	−13	2.0	75	71	Good
3-Oxa-1,8-octanediol						
Bis-2-ethylhexoate	Sl. hazy	<−60	8.1	74	71	Good
Ditoluate	Clear	−17	3.4	75	68	Very good
5-Oxa-1,9-nonanediol						
Dibenzoate	Incompatible	..	...	..	..	...
Dicaprylate	Sl. cloudy	<−60	5.8	73	70	Very good
Dioxa-1,10-decanediol						
Dicaprylate	Cloudy	<−60	5.6	72	72	Very good
3-Oxa-1,8-octanediol + dioxa-1,11-undecanediol						
Bis-2-ethylhexoate	Hazy	<−60	9.5	75	75	Good
Thiodiglycol						
Dibenzoate	Incompatible	..	..	..	..	...
Benzoate-caprylate	Clear	−44	1.7	72	69	Fair
Benzoate-2-ethylhexoate	Clear	−42	4.9	73	70	Good

[a] Original sample.

[b] After volatility test and another conditioning at constant temperature and humidity.

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