THE TECHNOLOGY OF SOLVENTS AND PLASTICIZERS

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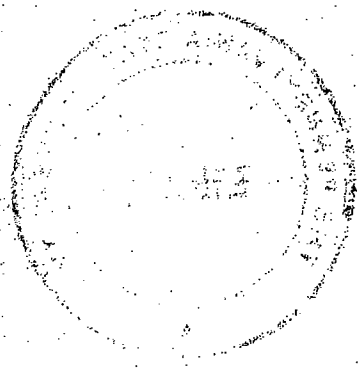

New York • JOHN WILEY & SONS, *Inc.*
London • CHAPMAN & HALL, *Limited*

Blumberg No. 5113
PLAINTIFF'S EXHIBIT 36

HARTOLDMON0030312

MGL.8
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Library of Congress Catalog Card Number: 54–9035

PRINTED IN THE UNITED STATES OF AMERICA

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perusal of the published literature clearly indicates that investigators favor the tensile-modulus method.

The basis of equivalence adopted in making the comparative measurements on resins of vinyl chloride type listed in Table 15.3 is that described in Reed's third paper.[28] This involves an elongation of 75 per cent at 1000 pounds per square inch on a tensile machine that applies a constant rate of loading of 15,000 pounds per square inch per minute. The room-temperature measurements given in Table 15.3 were made at or corrected to a temperature of 23° ± 1° C. and a relative humidity of 50 ± 2 per cent. All the measurements on plasticized specimens that are listed in this table, except those otherwise identified in footnotes, were made on specimens plasticized to this standard of equivalence. The amount of plasticizer required to provide this degree of flexibility is listed in Table 15.3 as plasticizer parts per 100 parts resin, or p.h.r.

(a) Permanence

Several concepts are included in the term permanence, and different tests are applied to evaluate each of these. The spew test, for example, determines whether the product is a primary or a secondary plasticizer. It may be stated quite generally that no compound will be retained permanently in a plastic specimen unless the compound is a solvent for and consequently is compatible with the resinous substance. The spew test is one method of establishing whether or not there is any exudation of plasticizer on aging 2 days at 60° C. and 100 per cent humidity.

Other aspects of permanence are volatility, water extraction, and oil extraction. The determination of the volatility of the pure plasticizer from an open dish is of qualitative value, but evaporation from a plasticized resinous specimen is influenced so much by polymer–plasticizer attraction and by the rate of diffusion within the plastic mass that a true evaluation of volatility must be made by means of tests on plasticized specimens. The results from two plasticizer-loss tests on specimens plasticized to the basis of equivalence described above are listed in Table 15.3. By one method,[26] the weighed test specimen is exposed to a current of air at 60° ± 1° C. for 10 days and reweighed. Since film thickness affects the results, the specimen dimensions are held to fairly close tolerances, and the results are corrected to a standard thickness of 0.004 inch. The test proposed by the Society of the Plastics Industry measures a combination of volatile loss and loss by absorption on porous particles. In the SPI method, the specimen is

placed inside a container in contact with activated carbon for 24 [illegible] at 70° C. This test is more rapid than the preceding one because activated carbon suppresses the partial pressure of the plasticizer in the atmosphere surrounding the specimen, thus preventing the establishment of equilibrium.

In the water-extraction test,[26] the weighed specimen is immersed in a bottle of water maintained at 23° ± 1° C. for 10 days. The water in the bottle is changed every 24 hours. At the end of 10 days' immersion the specimen is dried for 3 hours at 60° ± 1° C. in a ventilated oven and reweighed. The oil-extraction test[26] is similar to the water extraction test, except that mineral oil is used in place of water and the oil is changed only on the third and sixth days. In both cases the results are corrected to a specimen thickness of 0.004 inch.

Table 15.3 (see page 904) illustrates a number of observations related to permanence that are familiar to workers in the plastics field. For example, the less volatile simple plasticizers with the exception of tricresyl phosphate usually have the higher oil-extraction values. Almost all simple plasticizers are more readily extracted by oil than by water. When the oil extraction is low, however, the water extraction is likely to be relatively high. Good low-temperature behavior (see following section) is generally associated with high oil extraction. With resinous plasticizers, on the other hand, loss by volatilization or by oil or water extraction is greatly reduced but extreme low-temperature performance is sacrificed.

(*b*) Temperature Behavior

Temperature behavior is a very important characteristic of plasticized vinyl compositions. This is true because a great many plastic articles are designed as items of apparel or find application in connection with the daily pursuits of man, and hence are subject to the variations in temperature encountered in everyday life. In military applications the extremes are even greater because the articles may find service not only in the arctic or in the tropics but, in a matter of a few minutes, may be required to pass from high summer temperatures on the ground to subzero temperatures high in the air. The objective is to gain as nearly uniform performance as possible over a broad range of temperatures. A plasticizer that contributes this characteristic to a plastic is said to have "good low-temperature performance." This term is often applied loosely, but what is really meant is a relatively uniform mechanical properties over a broad temperature range. Different plasticizers vary widely in this respect. In general, plastic

TABLE 15.3 (*Continued*)

PROPERTIES OF COMMERCIALLY AVAILABLE PLASTICIZERS ARRANGED IN ORDER OF ASCENDING NUMBER OF CARBON ATOMS

No.	Name	Formula	Molecular Weight	Specific Gravity, 20° C.	Refractive Index	Viscosity, cp. at 20° C.	Solubility, % at 20° C.				Volatility of Free Plasticiser in Air, mg./sq. cm./hr.	
							In Water	Water in	In Mineral Oil	Mineral Oil in	212° F. (100° C.)	275° F. (191° C.)
	Simple Plasticizers (Continued)											
99	2-Ethylhexanoic acid diester of *N,N*-bis(2-hydroxyethyl)-2-ethylhexanamide	$C_{28}H_{53}O_5N$	484	0.956	1.458 at 20° C.	139.2	Insol.	0.5				12
100	Tri(*p-tert*-butylphenyl) phosphate	$C_{30}H_{39}O_4P$	495			f.p. 95–99.5 °C.						0.9
101	Glyceryl triricinoleate	$C_{57}H_{104}O_9$	933	0.959 at 25° C.	1.477 at 25° C.							
102	Glyceryl tri(acetylricinoleate)	$C_{63}H_{110}O_{12}$	1060	0.964	1.469 at 25° C.	271						0.7
	Resinous Plasticizers											
103	AROCLOR 1242, chlorinated biphenyl			1.378–1.388 at 25° C.	1.627–1.629 at 20° C.		Insol.	<0.1	*M*	*M*	2.50	146
104	FLEXOL plasticiser R-2H, polyester			1.055	1.469 at 20° C.	ca. 20,000	Insol.	1.0				0.5
105	G.E. 2557, polyester			1.028	1.459 at 20° C.	306						3
106	G.E. 2559, polyester			1.060	1.492 at 20° C.	4278						1
107	PARACRIL C, nitrile rubber			0.984								
108	PARAPLEX G-25, polyester		ca. 8000	1.06	1.470 at 20° C.	300,000						0.2

Comparison of Properties of Vinylite Resin VYNW-5 Specimens Plasticised to Equivalence[a]

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No.	Name	Plasticizer p.h.r. at 23° C., 75% Elongation, 1000 p.s.i.	Tensile Strength, p.s.i. at 23° C.	Ultimate Elongation, % at 23° C.	Shore Durometer A at 23° C.	Stiffness at 23° C., p.s.i.	T_f, °C.	Brittle Temperature, °C.	% Loss, 4-mil Film: 10 days, 60° C.	% Loss, 4-mil Film: 24 hours, 70° C.	% Extraction, 10 days, 23° C., 4-mil Film: Water	% Extraction, 10 days, 23° C., 4-mil Film: Oil	Spew, 2 days, 80° C., 100% Humidity [b]	Supplier [m]
	Simple Plasticizers (Continued)													
99	2-Ethylhexanoic acid diester of *N,N*-bis(2-hydroxyethyl)-2-ethylhexanamide	64	2730	327	63	650	− 3	−23	0.4	1.7	1.1	11.0	None	CCCC
100	Tri(*p-tert*-butylphenyl) phosphate												——	Dow
101	Glyceryl triricinoleate												——	Bak
102	Glyceryl tri(acetylricinoleate)	68.6 [c,g]							1.4		2.5	9.5	None	Bak
	Resinous Plasticizers													
103	Aroclor 1242, chlorinated biphenyl	56.2 [h]							4.5		0.6	0.6	None	Mon
104	Flexol plasticizer R-2H, polyester	90	3080	360	57	440	+2	−10	0	0	0	2.4	None	CCCC
105	G.E. 2557, polyester	72	2730	310	63	580	− 2	−18	0.9	3.5	3.1	17.0	Very slight	GE
106	G.E. 2559, polyester	90 [i]	2110	215	72	740	6	− 6	0.6	2.3	2.7	7.1	Very slight	GE
107	Paracril C, nitrile rubber	106	2500	410			+ 7	−54	0.5		0.2	0.6	None	Nau
108	Paraplex G-25, polyester	82	2600	310	60	480	− 1	−25	0.2		1.0	0.6	None	RH

[a] 1000 p.s.i. tensile modulus at 75% elongation at 23° C. on tensile machine with constant rate of loading of 15,000 p.s.i. per minute.
[b] Dash (——) indicates no data available.
[c] 100% elongation, 1000 p.s.i., constant rate of loading of 810 p.s.i. per minute. See Reed.[26]
[g] Mixture of 0.9 part plasticizer to 1 part tricresyl phosphate.
[h] Only composition tested, does not yield standard elongation.
[i] Highest plasticizer content tested. Elongation at 1000 p.s.i. = 64%.
[m] For key to supplier abbreviations see page 903.

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The chlorinated paraffins are not recommended for nitrocellulose lacquers. Figure 16.39 presents the stiffness-temperature relations of Vinylite resin VYNW-5 plasticized with mixtures of 1 part chloroparaffin 40 to 3 parts di(2-ethylhexyl) phthalate. The reference composition is 68 p.h.r.

Chlorinated Biphenyls

Chlorinated Biphenyl (——) mol. wt. ——

Properties: b.r. 330–370, fl.p. 380, fi.p. none, p.p. −7, ρ_{25} 1.447–1.457, n_{20} 1.627–1.629. Soluble in organic solvents and hydrocarbons, insoluble in water. Compatible with most commercially available rubbers and resins except cellulose acetate.

Several chlorinated biphenyls are commercially available, differing from each other in physical appearance, viscosity, and compatibility relationships. In general, these products improve alkali resistance in nitrocellulose lacquers, and by themselves or in combination with waxes, tars, and asphalts serve in impregnation and moistureproofing operations. Aroclor 1242 was chosen as the representative of this class of plasticizers to be discussed here because this particular compound appears to have some merit in connection with vinyl plastics. Aroclor 1242 is a primary plasticizer for resins of vinyl chloride type that contributes to flame retardation and affords very low losses by volatilization and by oil or water extraction. The low-temperature performance of all the chlorinated biphenyls is poor.

These highly chlorinated compounds have caused dermatological difficulties known as chloracne, and, when absorbed repeatedly by inhalation or through the skin, they have been blamed for fatalities from liver damage. Industrial applications should be planned to prevent human contact and absorption.

Miscellaneous Chlorinated Products

(a) Esters

Methyl Pentachlorostearate ($C_{19}H_{33}O_2Cl_5$) mol. wt. 471

$$C_{17}H_{30}Cl_5COOCH_3$$

Properties: f.p. −39, fl.p. 328, fi.p. 485, p.p. −18, ρ_{20} 1.204, η_{20} 975, n_{20} 1.497. Soluble in organic solvents and hydrocarbons, insoluble in water. Compatible with many resinous substances and rubbers. Not compatible with nitrocellulose, cellulose acetate, or polyvinyl butyral.

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