

Plasticizers

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THIS paper is divided into three main parts. The first part is devoted to a general discussion of plasticizers, what they are, what they are expected to accomplish, how they function, and some background material on internal plasticization. The



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second part is devoted to a discussion of specific plasticizers and plasticizer types used mainly with polyvinyl chloride, the synthetic plastic material which consumes the largest quantity of plasticizers. The third part is confined to plasticizers from fats and attempts to show how fats can be used both for internal and external plasticization. Those of us who are working on the problem of finding industrial uses for our surplus fats know that we must focus our attention on those chemical fields which consume large quantities of organic chemicals. One of the largest and fastest growing consumers of organic chemicals is the synthetic plastics industry. This industry alone uses over three billion pounds of chemicals annually. Many synthetic plastics however, representing huge actual and potential tonnage, are hard, inflexible, high-melting, and difficult to process, and they require modification to make them suitable for applications where flexibility, toughness, and elasticity over a wide range of temperature are prerequisites. The main technique used to modify the properties of these brittle, horny substances is the addition of plasticizers or, as they are sometimes called, softening or modifying agents.

General Discussion of Plasticizers

What are plasticizers? Plasticizers are usually polar compounds, occasionally low melting solids but most commonly high boiling liquids, which are added to synthetic plastics for the purpose of modifying the physical properties of the synthetic resins and to develop new, improved properties not present in the synthetic resins themselves. The molecular weights of plasticizers are much lower and of an entirely different order of magnitude than those of the synthetic resins to which they are added. In general, as suggested earlier, the major function of a plasticizer is to convert the plastic from a hard, brittle, inflexible, high-melting, substance to a softer, flexible, lower-melting but tough material which can be subsequently processed in a satisfactory manner. Large proportions of plasticizers, sometimes exceeding 50% of the total weight, are frequently used in resin formulations. In fact, a synthetic resinous composition for use in producing flexible articles has been humorously defined as a high-boiling organic liquid to which sufficient polymer has been added to give structural rigidity.

Examples of useful plasticizers are dioctyl phthalate, tricresyl phosphate, and epoxidized soybean oil. The first plasticizer to be used commercially, apparently, was camphor, employed by Hyatt in 1868 with nitrocellulose. Camphor is still utilized to a limited extent at the present time.

Although many secondary properties may also be required, the basic attributes of a good permanent plasticizer are: a) that it be compatible with the material it is to plasticize, and b) that its volatility be low. As used in the plastics field, compatibility means the ability of the plasticizer and the plastic to mix and remain homogeneously dispersed in one another. Frequently substances are found which appear to be miscible with the plastic but, on standing, exudation occurs. Compatibility may be determined by solution casting a film and examining the dry film for clouding, streaking, exudation, or crystallization. Compatibility can also be determined by milling the resin with increasing amounts of plasticizer and visually examining the milled sheet for exudation, stickiness, or oiliness. The time, temperature, and ease of milling are often indications of compatibility. Generally speaking, a highly compatible plasticizer will form a clear homogeneous sheet in a shorter space of time than will a less compatible plasticizer.

After it has been determined that a plasticizer is compatible, it must then be evaluated on the basis of the performance. The efficiency of a plasticizer is the performance of the finished product measured against the concentration of the plasticizer required to obtain the desired properties.

Among the most important characteristics employed to evaluate the efficiency of a plasticizer are tensile strength, elongation, and modulus of the plasticized composition. Tensile strength is the load in pounds per square inch supported by the sample at the moment of rupture. Percentage elongation is the ratio of the length of the sample at the moment of rupture to the initial length. Modulus is a measure of the ease or difficulty with which a plastic can be elongated. Modulus is reported in pounds per square inch; the lower the modulus, the greater the ease of elongation. These characteristics are important because they help define the toughness and range of structural utility of a plasticized composition. An efficient plasticizer can be used in low enough concentration so that the elongation of the composition is increased but the tensile strength is not degraded below the useful point. After all, we know that many plasticized compositions must be able to withstand severe pulling and stretching.

Other characteristics which must frequently be determined on a plasticized composition in evaluating the plasticizer, particularly for specialized uses, are low temperature flexibility, hardness, weather and solvent resistance, electrical properties, high temperature and light stability, flame-resistance, abrasion resistance, flow characteristics, toxicity, color and odor, and last but of paramount importance, price. For a plasticizer to achieve widespread use it must be cheap, selling for about 40c per pound or less. Al-

though price is listed at the end, the importance of a low price cannot be overemphasized.

Since plasticized compositions depend upon the plasticizer for so many of their desirable properties, it is essential that the plasticizer be permanent for the service life of the product. The permanence of a plasticizer is a combination of its volatility, solvent, oil and water resistance, resistance to migration, and heat and light stability.

In general, plasticizers have molecular weights in the range of 300-3,000 and for most practical purposes can be classified as non-volatile. Low vapor pressure at high temperatures is one assurance that the plasticizer will not evaporate from the plasticized composition. This is especially important in films and coatings in which a large surface area is present in relation to the mass of the composition. Although high-boiling point alone is not a sufficient criterion for non-volatility over the wide range of temperatures encountered in use, as a rough rule of thumb a substance should preferably have a boiling point that exceeds 200°C. at 1 mm. pressure to be sufficiently non-volatile.

Many plasticized compositions must be used in contact with oil or hydrocarbon solvents. For example, shoe soles and floor coverings must be oil- and solvent-resistant for long service life. This requirement demands that the plasticizer resist solubilization in oil or organic solvents likely to be encountered in service.

In many applications plastic products come in contact with water. Unless the plasticizer has extremely low solubility, it will be leached out causing loss of flexibility, swelling or shrinkage, and possibly clouding and crystallizing. Plasticizers should also be resistant to removal by aqueous soap or detergent solutions.

When two plastic surfaces are in contact with one another, plasticizer migration is the tendency of the plasticizer in one to leave the composition and enter the other. The amount of plasticizer migration is directly related to the temperature, pressure, and time of contact, and, of course, the structure of the plasticizer. It is desirable that vinyl compositions used for apparel or accessories, such as handbags, that may be in contact with varnished or lacquered surfaces be plasticized with compounds that are essentially non-migratory. In electrical applications, also, non-migratory plasticizers are important. Polyethylene, for example, which is widely used for insulation, is frequently jacketed with plasticized vinyl resin.

It should be emphasized that the perfect plasticizer has not yet been discovered. A plasticizer may be outstanding in its low temperature characteristics yet show poor or average migration tendencies. Another plasticizer may have excellent migration characteristics yet be relatively inefficient in modifying the over-all properties of the plastic. All commercial plasticizers represent a compromise based on price and availability, and plasticizing or modifying efficiency. Since no plasticizer is perfect, it is common commercial practice to employ mixtures. Plasticizers are selected on the basis of modifying characteristics which are better than average (preferably outstanding) and cost per pound.

Just how do plasticizers function? There is still considerable argument regarding the actual mechanism of plasticizer action, and time does not permit a detailed discussion of the various view-points. As is well known, thermoplastic resins are long-chain compounds. The binding forces between these chains are

the primary cause of the stiffness and high-melting point of many synthetic resins. These binding forces which vary in number and magnitude from resin to resin, are often referred to as van der Waal forces or secondary bonds. A plasticizer reduces or overcomes these intermolecular forces of attraction by placing itself between the chains, thus increasing the distance over which these forces must operate. In addition, the plasticizer may act as a lubricant, permitting the chains to slide and bend more readily. Thus a plasticizer imparts increased elasticity at much lower temperatures. The extent of plasticization depends in part upon the molecular structure of the polymer and in part upon the molecular structure of the plasticizer.

Up to this point we have discussed external plasticizers only, that is, substances which are added to a synthetic resin after it is formed. Since external plasticizers are mechanically admixed with synthetic resins, there are a variety of ways in which the plasticizer can be lost during use. As mentioned earlier, one is by evaporation although this can be largely overcome by using plasticizers with sufficiently low vapor pressures over the use-range of the plasticized composition. Another way in which plasticizers can be lost is by migration to the surface of the plasticized composition followed by mechanical removal, as by wiping or rubbing, or removal by solvents, water, or detergent solutions. The synthesis of polymeric and other relatively non-migratory plasticizer types has largely overcome this problem. Aside from the drawback of plasticizer loss, there are also important cases where plasticizers preferably should be absent, yet flexible plastic materials are required. Examples are vinyl coatings for polyethylene used as an insulator on coaxial cable, flexible vinyl articles which are to be coated with metals under high vacuum for decorative purposes, and food-packaging materials.

This preliminary discussion brings us to the subject of internal or structural plasticization. Since plasticization has already been defined as a process which reduces intermolecular attractive forces, it follows that if we co-polymerize one monomer, such as vinyl chloride, with another monomer, such as vinyl stearate, the long-chain of the co-monomer will serve to separate the polyvinyl chloride chains, intermolecular attractive forces will have been reduced, and we will have accomplished plasticization of the polymer. Unlike external plasticizers, internal plasticizers cannot be lost by evaporation, bleeding, or leaching. Their effect is permanent.

Plasticizers for Polyvinyl Chloride

The next part of the paper will be devoted to polyvinyl chloride and the plasticizers which are commonly used with this important commercial plastic. Approximately 400,000,000 pounds of polyvinyl chloride were produced in the United States in 1952. Flexible compositions represent by far the greatest outlet today for polyvinyl chloride, and approximately 200,000,000 pounds of plasticizers were required to modify the properties of the rigid polyvinyl chloride. Table I lists the most important plasticizers used with polyvinyl chloride and shows production and consumption statistics for 1952 in the United States.¹ Of somewhat

¹The preliminary figures for 1953 recently became available. Sale of plasticizers increased about 15% over 1952. Major changes were in the increased use of octyl decyl phthalate, tricresyl phosphate, dibutyl phthalate, dicapryl phthalate, diethyl phthalate, di-n-octyl and diisooctyl phthalates, and oleic esters. Stearic and lauric esters dropped considerably, but this resulted from better classification as surface-active agents rather than from decreased use as plasticizers.

TABLE I
United States Production and Sales of Plasticizers—1952
(U. S. Tariff Commission, Preliminary Report)

Chemical	Production 1000 lb.	Sales		
		Quantity 1000 lb.	Value \$1000	Unit Value per lb.
Grand Total.....	266,957	201,566	\$75,039	\$0.37
Plasticizers, Cyclic				
Total.....	194,362	144,539	51,126	.35
Phosphoric acid esters.....	23,789	16,485	5,667	.34
Tricresyl phosphate.....	18,031	16,485	5,667	.34
Triphenyl phosphate.....	5,758
Phthalic anhydride esters.....	149,826	105,237	38,151	.36
Dibutyl phthalate.....	17,881	12,475	4,224	.34
Dicapryl phthalate.....	5,246	5,220	1,804	.35
Diethyl phthalate.....	12,138	9,193	2,512	.27
Di(2-methoxyethyl) phthalate [Di(methyl cellulose) phthalate].....	1,576
Dimethyl phthalate.....	2,901	3,005	837	.28
Diocetyl phthalates.....	86,857	54,320	20,592	.38
Di-2-ethylhexyl phthalate.....	63,236	38,082	14,510	.38
Di-isooctyl and di-n-octyl phthalates.....	23,621	16,238	6,082	.37
All other ^a	23,227	21,024	8,182	.39
All other cyclic plasticizers ^b	20,747	22,817	7,308	.42
Plasticizers, Acyclic				
Total.....	72,595	57,027	23,913	.47
Adipic acid esters.....	7,277	5,061	2,388	.44
Di-2-ethylhexyl adipate.....	3,204	1,886	826	.32
Di-isooctyl adipate.....	1,125	899	399	.44
All other ^c	2,948	2,276	1,163	.51
Lauric acid esters.....	1,050	959	356	.37
Glycerol monooleate.....	164
Polyethylene glycol mono- and dilaurate.....	233	224	88	.39
1,2-Propylene glycol monooleate.....	181
All other ^d	472	735	268	.36
Oleic acid esters.....	6,645	3,617	1,132	.31
Diethylene glycol monooleate.....	439	329	115	.35
Glycerol monooleate.....	662	663	222	.33
Polyethylene glycol monooleate.....	559	203	78	.38
All other ^e	4,985	2,422	717	.30
Phosphoric acid esters ^f	8,991	5,779	2,664	.46
Ricinoleic (acetylricinoleic) esters ^g	4,295
Sebacic acid esters.....	5,653	4,652	3,661	.79
Dibutyl sebacate.....	2,215
Di-isooctyl and di-2-ethylhexyl sebacate.....	3,004	3,056	2,253	.74
All other ^h	1,434	1,596	1,408	.88
Stearic acid esters.....	16,245	14,681	4,402	.30
Butyl stearate.....	1,802	1,618	394	.24
Diethylene glycol monostearate.....	458	416	114	.27
Ethylene glycol monostearate.....	310	322	107	.33
Glycerol monostearate.....	8,823	7,789	2,337	.30
Propylene glycol monostearate.....	186	172	64	.37
All other ⁱ	4,666	4,364	1,366	.32
All other acyclic plasticizers ^j	22,519	22,278	9,310	.42

^a Includes data for butylbenzyl, castor oil, diallyl, and dicyclohexyl phthalates, and for phthalic anhydride esters of cellosolves, phenols, and polyhydric alcohols.

^b Includes data for synthetic camphor, coumarone-indene, toluene-sulfonamides, phosphoric and sebacic acid esters, tetrahydrofurfuryl oleate, and other cyclic plasticizers.

^c Includes data for adipic acid esters of cellosolves and polyhydric alcohols.

^d Includes data for lauric acid esters of methyl and butyl alcohols, and of glycols and cellosolves.

^e Includes data for butyl, butyl cellosolve, methyl and propyl oleates, glyceryl trioleate and other esters of oleic acid.

^f Includes data for tributyl, triethyl, trioctyl, and tributyl (cellosolve) phosphates.

^g Includes data for ricinoleic and acetylricinoleic acid esters of mono-, di-, tri-, and polyhydric alcohols, and cellosolves.

^h Includes data for diamyl, dicapryl, dimethyl, dinonyl sebacates, and for sebacic acid esters of cellosolves.

ⁱ Includes data for stearic, monohydroxystearic, and chlorostearic acid esters of mono-, di-, and polyhydric alcohols, and cellosolves.

^j Includes data for butyl and isopropyl myristates, diethyl and isopropyl maleates, glycerol and glycol esters of fatty acids, and esters of azelaic, citric, palmitic, pelargonic, tartaric, and other acids.

over 200 million pounds of plasticizers sold in 1952 for about \$75 million, about 72% or 144 million pounds were derived from cyclic compounds and consisted mainly of phthalate esters. Tricresyl phosphate (16.5 million pounds), dioctyl phthalates (54.3 million pounds), and about a dozen other phthalate esters (51 million pounds) took care of the vast bulk of the business. The average price of these cyclic plasticizers

was \$0.35 per pound, and gross sales amounted to about \$51 million. The remaining 28% or 57 million pounds of plasticizers were acyclic or straight-chain esters (5 million pounds), lauric acid esters (1 million pounds), oleic acid esters (3.6 million pounds), phosphoric acid esters (5.8 million pounds), ricinoleic esters (4 million pounds), sebacic acid esters (4.6 million pounds), stearic acid esters (14.7 million pounds), and many others (22 million pounds). The average price of these, \$0.47 per pound, was considerably higher than that of the cyclic plasticizers and largely accounts for the much lower sales. Total sales of straight-chain plasticizers amounted to about \$24 million.

Some of the main applications for plasticized polyvinyl chloride are electric wire and cable coverings, pliable thin sheeting, such as shower curtains, rain wear and inflated toys, coatings for fabrics and paper, shoe soles, floor coverings, food-packaging materials, and numerous other applications in every-day use. It should be borne in mind that although polyvinyl chloride is the most important synthetic resin employing plasticizers today, this picture may change radically as new synthetic resins are discovered and as new plasticizers for well-known resins are developed.

The most important class of plasticizers by far for polyvinyl chloride are esters. The two most important of these are di (2-ethylhexyl) phthalate, usually referred to as dioctyl phthalate or DOP, and tricresyl phosphate or TCP. These compounds, of course, are not obtained from fats and although they have certain drawbacks, they are cheap and plentiful, and they represent an excellent compromise in the many important properties desired in a plasticizer for all-round use.

On the other hand, esters of straight-chain dibasic acids, such as sebacates, azelates, and adipates, are among the best available for low temperature flexibility. As you know, sebacic acid is obtained from castor oil by fusion with alkali, and azelaic acid, a potentially cheap dibasic acid, is obtained from oleic acid by ozonolysis. Esters of glycols with fatty and other acids also impart good low-temperature characteristics to polyvinyl chloride, but, in general, the requisite C₄-C₆ glycols are either somewhat too expensive or not available. The polyethylene glycols, which are the compounds used commercially, give esters retaining some of the good low temperature flexibility properties, but compatibility is decreased and water sensitivity increased. Triethylene glycol caprylate or isohexoate, for example, is a useful and efficient low temperature plasticizer.

Most polymeric or resinous plasticizers are prepared by condensing a dibasic acid, such as sebacic or azelaic acid, with a glycol. A monobasic fatty acid is sometimes added to control the molecular weight, the preferred range of which is usually 1,000-3,000. Polymeric plasticizers are non-volatile and are outstanding in resistance to migration and extraction. Their efficiency, compatibility, and low temperature characteristics however are usually not as good as those of the monomerics.

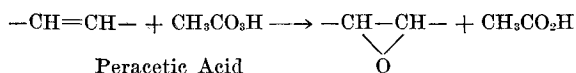
Plasticizers from Fats

Fats, or compounds simply or directly derived from them, are inexpensive for the most part, they have low vapor pressures and good water resistance, and they impart flexibility to materials with which they

are miscible. Unfortunately fats or compounds which are predominantly fatty have low compatibility with polyvinyl chloride. It is this characteristic which has prevented the large-scale utilization of fats in polyvinyl chloride. Up to within a few years ago, where compounds derived from fats achieved any reasonable use, they were "secondary" plasticizers rather than "primary" or true "solvent" plasticizers. By way of definition, it should be pointed out that a primary or solvent type plasticizer is one which can be used as the sole plasticizer even in relatively high percentages of the total formulation. Fat-derived products have been used to provide hand and drape to vinyl sheeting, to serve as lubricants in milling to reduce milling temperatures, and, if the price is satisfactory, to serve as diluents for more expensive plasticizers. Ricinoleates are the best known and possibly the most widely used secondary plasticizers derivable from fats, and they possess good low temperature characteristics. Examples are methyl acetyl ricinoleate, butyl acetyl ricinoleate, and propylene glycol diacetyl ricinoleate. Esters of oleic, palmitic, and stearic acid have also been used as secondary plasticizers. The first generally has better heat stability and compatibility. These esters frequently impart good low temperature and processing qualities to polyvinyl chloride. Examples are methyl cellosolve oleate, diethylene glycol monooleate, glyceryl monooleate, polyethylene glycol monooleate, dimethyl glycerol ether oleate, phenyl oleate, tetrahydrofurfuryl oleate, glyceryl monostearate, benzyl stearate, diethylene glycol monostearate, ethylene glycol monostearate, phenyl stearate, butyl stearate, and iso-octyl palmitate. It should be noted that ether linkages and cyclic groups seem to improve compatibility. Chlorinated alkyl stearates have also been suggested for use as plasticizers. Three to six chlorine atoms per molecule are apparently required to achieve sufficient compatibility, but the introduction of the highly polar chlorine atoms increases dielectric loss. Acetoglycerides have also been suggested as secondary plasticizers.

About three years ago a new class of fatty plasticizer for polyvinyl chloride was put on the market, and its consumption has grown rapidly. This plasticizer was epoxidized soybean oil, and recently epoxidized butyl oleate, hexyl oleate, and octyl oleate became commercially available. For the first time compounds derived directly from fats show promise as primary plasticizers for polyvinyl chloride and can compete with dioctyl phthalate and other plasticizers per-wise and performance-wise. Before discussing epoxidized soybean oil and other epoxidized fatty materials, it would be well to discuss the epoxidation reaction briefly.

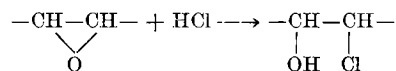
About 10 years ago it was shown in our laboratory that the unsaturated centers of fatty materials could be converted in excellent yield to epoxide groups by reaction with organic peracids illustrated in the equation below:



Commercially the practice is to treat the unsaturated compound with hydrogen peroxide of approximately 50% strength in the presence of small amounts of acetic or formic acid. The aliphatic acid acts as the oxygen carrier as well as the reaction medium. We demonstrated that the epoxidation reaction is a general one and is applicable to unsaturated fatty acids,

esters, including glycerides, alcohols, amides, and other classes of long chain compounds.

Why are epoxidized fatty materials becoming increasingly popular for use with polyvinyl chloride? Chlorine-containing vinyl resins, of which polyvinyl chloride is by far the most important, decompose with the liberation of hydrogen chloride when they are exposed to heat and/or light. The hydrogen chloride liberated seems to speed up further decomposition when oxygen is present, and within a short time the plastic material is discolored, brittle, weak, and of little value. Epoxidized fatty materials react rapidly and quantitatively with hydrogen chloride, as the equation shows:



Therefore the small amount of hydrogen chloride which is liberated during the early stages of decomposition of polyvinyl chloride is quickly neutralized, and the subsequent accelerated decomposition is checked before it can get started. In addition to their main characteristic of stabilizing polyvinyl chloride, epoxidized fatty materials are compatible with polyvinyl chloride, they have low vapor pressures and excellent resistance to migration and water.

As discussed above, epoxidized soybean oil was the first stabilizing plasticizer to be used commercially. Soybean oil was chosen for epoxidation because it was plentiful and cheap. Its compatibility with polyvinyl chloride is only fair because a large percentage of incompatible components are present in the triglyceride molecules and the molecule is large and bulky. Temperature changes, in particular, cause exudation. A recent growing trend in the development of epoxidized fatty materials as stabilizing-plasticizers is the use of simple esters, such as butyl, hexyl N, or octyl epoxystearate. The fatty acid portion is derivable generally from inedible animal fats. The compatibility of these epoxy esters with polyvinyl chloride is good, the formulations have excellent low-temperature characteristics, and it has been proposed that they be used as primary plasticizers as well as for their excellent stabilizing effect. Other epoxy esters for which evaluation data are reported in the literature are methyl epoxystearate, epoxidized methyl and butyl esters of cottonseed and soybean oil acids, epoxidized octyl, tetrahydrofurfuryl and diethylene glycol monobutyl ether esters of soybean oil acids, epoxidized ethylene glycol monobutyl ether esters of oleic acid, epoxidized methyl esters of dimer acids, diethylene glycol diepoxystearate, benzyl epoxystearate, cyclohexyl epoxy stearate, and phenyl epoxystearate.

Recent research in our laboratory has resulted in the development of a new class of primary epoxy stabilizing plasticizers. These are epoxidized monoglyceride diacetates, and they are derived from inexpensive and plentiful fats such as soybean and cottonseed oil, tallow, lard, and grease. They can be prepared by interesterification of fat triglyceride and triacetin, followed by epoxidation of the monoglyceride diacetate. The monoglyceride diacetates can also be prepared by the reaction of fats with glycerol to yield monoglycerides, followed by acetylation with acetic anhydride, but the interchange reaction is much more convenient. Epoxidation of the double bonds of the fat acid group in the monoglyceride diacetate yields epoxidized monoglyceride diacetates. These are effi-

