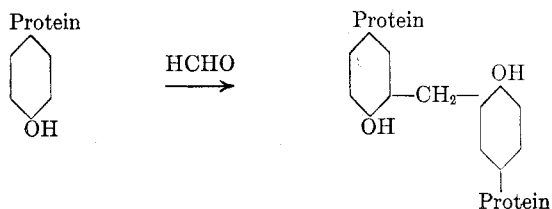


The low shrinkage of treated zein fibers in boiling acids and the resulting high strengths indicate the formation during the cure of irreversible crosslinks between the protein molecules. Protein-formaldehyde reactions formerly postulated do not account for this irreversible stabilization of zein fiber. Fraenkel-Conrat and Olcott (4) reported irreversible crosslinking between protein groups by a Mannich type of reaction. The absence of amino groups in zein excludes this possibility unless it is assumed that ammonia of hydrolysis is first converted to dimethylamine which then condenses with two active $=C$ -groups. Such a series of reactions seems to be improbable because of the rapidity of the cure.

The well-known phenol-formaldehyde reaction readily occurs under conditions of the cure. Though usually not considered as a possible crosslinking mechanism for proteins, the reaction would explain the tying of two protein chains together with an acid resistant methylene linkage between their tyrosine residues.



That tyrosine is involved in at least part of the mechanism is supported by the following facts:

1. The cure reduced the intensity of color of the Millon test on the fiber.
2. The cure was not very effective on partially iodinated fiber.
3. Only a relatively small amount of tyrosine was isolated from an acid hydrolyzate of the cured protein.
4. The solubilities and acid resistance of other proteins such as gliadin, casein, and soybean protein which contain appreciable amounts of tyrosine were markedly modified by the cure; whereas gelatin, which contains only traces of the amino acid, was not affected.

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RECEIVED September 19, 1949. A patent application by C. B. Croston, C. D. Evans, L. L. McKinney, and J. C. Cowan covering the results of this work has been filed in the U. S. Patent Office and assigned to the Secretary of Agriculture.

Creep Behavior of Plasticized Polyvinyl Chloride

LIQUID POLYMER PLASTICIZERS

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Studies on the creep behavior of vinyl chloride resin plasticized with liquid polymers derived from common vinyl monomers are reported. The various chemical factors that influence the formation of liquid vinyl polymers are described. In general, efficient chain transfer reagents such as carbon tetrabromide may be used successfully with the acrylate monomers to yield liquid polymers, whereas "degradative" chain reagents of the allyl type yield liquid polymers with a variety of vinyl monomers when used in copolymerizing systems. A number of the liquid polymers are compared, by tensile creep, with commercially used plasticizers; their plasticizing efficiency, under certain conditions of temperature and concentration, was found to be quite satisfactory.

THE development of polymeric plasticizers constitutes one of the recent important advances in the field of plasticizers for vinyl resins. As typical examples, one might consider the high molecular weight polyesters (7) and nitrile rubbers (9) which have attracted considerable attention as useful plasticizers because of their outstanding resistance to volatile loss and extraction and because of their low marring action.

There have been no systematic attempts reported, however, on the preparation of low molecular weight polymers of the common vinyl monomers, from the point of view of employing such ma-

terials as plasticizers. In the studies reported here the established principles of chain transfer and polymerization kinetics were applied to the preparation of a series of liquid vinyl polymers and copolymers, and their relative merits as plasticizers for vinyl resins were evaluated by simple tensile creep and physical property measurements. Preparation of viscous liquids rather than low molecular weight solids was always strived for since it was felt that in this way maximum plasticizing efficiency could be attained, consistent with the requirements for low volatility.

EXPERIMENTAL PROCEDURE

The procedure employed in the present studies for preparation of plasticized films of polyvinyl chloride (Geon 101) and vinyl chloride-acetate copolymer (VYNW) is identical to that described by Aiken, Alfrey, Janssen, and Mark (1). Films were cast containing 25 and 45% plasticizer. The methods of these authors were also used for measurement and calculation of tensile creep. The creep tests were carried out in the temperature range -20° to 50° C. and the data were plotted as strain divided by stress (γ/S), square cm. per dyne, against logarithmic time in seconds. Care was taken that the extent of creep did not exceed 10% throughout each run in order to obviate corrections for the changes in cross-sectional area of the samples. Measurements of ultimate tensile strength and elongation at break of the plasti-

TABLE I. MONOMERS EMPLOYED IN PREPARATION OF LIQUID POLYMERS

1. <i>n</i> -Butyl acrylate	6. Allyl chloride
2. 2-Ethyl hexyl acrylate	7. Vinyl chloride
3. Lauryl methacrylate	8. Vinyl acetate
4. Methacrylonitrile	9. Styrene
5. Acrylonitrile	10. Allyl acetate (prepared by laboratory synthesis)

cized films were carried out at room temperature with an inclined plane Scott tester.

In the preparation of the liquid polymers, the starting monomers were first purified to remove impurities and inhibitors. Generally, this procedure consisted of alkali and water washing, drying under anhydrous sodium sulfate, and then distilling the monomer to collect the middle fractions. Those monomers affected by alkali were not washed but were simply vacuum distilled to remove inhibitors.

Polymerizations were carried out in small sealed tubes, containing 25 ml. of reactants, for various times and temperatures. The products obtained were washed twice with methanol-water mixture (70:30) and then stripped to remove volatile components under nitrogen (2 to 4 mm.) at 130° to 140° C. As some of the materials discolored in this temperature range it was necessary in such instances to carry out prolonged stripping at lower temperatures until all odor was essentially removed. The number average molecular weight of each stripped product was obtained cryoscopically, using benzene as solvent.

PREPARATION OF LIQUID VINYL POLYMERS

During the preparation of liquid polymers, the ten vinyl monomers listed in Table I were studied. Although it is known that high temperatures and high catalyst concentrations favor the formation of low molecular weight polymers, these two factors alone are not necessarily sufficient nor conducive to the preparation of suitable products. Under extreme conditions of reaction temperature and catalyst concentration, the exotherm of the polymerization reaction presents an element of danger; in addition it is quite likely that simultaneous degradation of the polymer may occur leading to the formation of highly discolored reaction products. To bring about liquid polymer formation under mild conditions of polymerization and in as simple a manner as possible, chain transfer reagents (8) were employed. From a variety of chain transfer reagents studied, carbon tetrabromide was one of the most effective, based on minimum amounts required to form liquid polymers. The efficiency of carbon tetrabromide as a chain transfer reagent undoubtedly arises from the high lability of the bromine atoms.

Several of the monomers studied did not yield liquid polymers with chain transfer reagents, despite their low molecular weights. Apparently the physical state of these products is such that even the lowest molecular weight species are solids rather than liquids. In order to prepare useful products with these materials the polymerization method was modified. In place of chain transfer

reagents, "degradative" chain transfer monomers of the allyl type (4) were copolymerized with the vinyl monomer. By varying the amount of allyl component in the comonomer mixture, polymeric products ranging from solids to liquids could be obtained. The term "degradative" chain transfer has been applied by Bartlett and Altschul (4) to specify the chain transfer process occurring in the polymerization of allyl chloride and allyl acetate wherein the monomer itself serves as transfer reagent. In the copolymerization reactions the presence of the allyl comonomer served a twofold purpose. It functioned first as a chain transfer reagent and thus decreased the molecular weight of product formed; secondly, by entering into the copolymer chain, it brought about a change in physical state, to the extent that the products formed were liquids.

Several pertinent studies have been reported on the reactions of allyl compounds with vinyl monomers. In a recent patent Eugene, Moffet, and Smith (6) noted that soft polymers may be obtained by polymerization of a mixture of allyl chloride (or methallyl chloride) and vinyl chloride, employing benzoyl peroxide as catalyst. These authors recommend the use of the product formed as an interlayer for safety glass. In 1946 Alfrey and Harrison (2) studied the copolymerization of allyl chloride and styrene and showed that a real copolymer is formed, but nothing was reported concerning the molecular weight of the polymer. The first detailed study of low molecular weight vinyl polymers was that of Bartlett and Altschul (4) on allyl monomers, but their main emphasis was directed toward the kinetics of the reactions rather than use of the final products.

The results of these investigations on the preparation of liquid

TABLE II. PROPERTIES OF LIQUID POLYMERS PREPARED FROM ONE-COMPONENT MONOMER SYSTEMS EMPLOYING CARBON TETRABROMIDE CHAIN TRANSFER REAGENT

(Catalyst, 1% benzoyl peroxide; polymerized at 75° C. for 72 hours)

Code	Monomer ^a	Transfer Reagent, Weight %	Yield, %	Consistency	Compatibility with Vinyl Chloride (Geon 101) Resin	Molecular Weight
P ₁	2-Ethyl hexyl acrylate	3	80	Flows	Incompatible	680
P ₂	<i>n</i> -Butyl acrylate	3	90	Flows	Compatible	650
P ₃	Lauryl methacrylonitrile	3	80	Viscous	Compatible	700
P ₄	Allyl acetate	3	40	Flows	Compatible	580
P ₅	Allyl chloride	3	40	Flows	Compatible	380
P ₆	Styrene	6	80	Very viscous	Compatible	720

^a Acrylonitrile, vinyl chloride, and vinyl acetate did not give liquid polymers under similar conditions with 6% CBr₄.

TABLE III. PROPERTIES OF LIQUID COPOLYMERS PREPARED FROM COMONOMER SYSTEMS EMPLOYING DEGRADATIVE CHAIN TRANSFER MONOMER

(Polymerized at 75° C. for 72 hours)

Code	Weight Fraction Monomer I	Weight Fraction Monomer II (Allyl Chloride) ^a	Catalyst, %	Yield, %	Copolymer Consistency	Compatibility with Vinyl Chloride (Geon 101) Resin	Molecular Weight
C ₂	Vinyl chloride, 0.3	0.7	Acetyl peroxide, 2	68	Slightly viscous	Compatible	630
C ₄	<i>n</i> -Butyl acrylate, 0.7	0.3	Acetyl peroxide, 2	80	Flows	Compatible	540
C ₇	Vinyl acetate, 0.7	0.3	Benzoyl peroxide, 2	80	Flows	Compatible	600
C ₁₄	Allyl acetate, 0.8	0.2	Benzoyl peroxide, 1	40	Flows	Compatible	470
C ₁₆	2-Ethyl hexyl acrylate, 0.8	0.2	Benzoyl peroxide, 1	70	Slightly viscous	Partially compatible	600
C ₁₇	Lauryl methacrylate, 0.8	0.2	Benzoyl peroxide, 1	80	Slightly viscous	Compatible	630

^a Under similar conditions styrene and methacrylonitrile did not give suitable liquid products with allyl chloride.

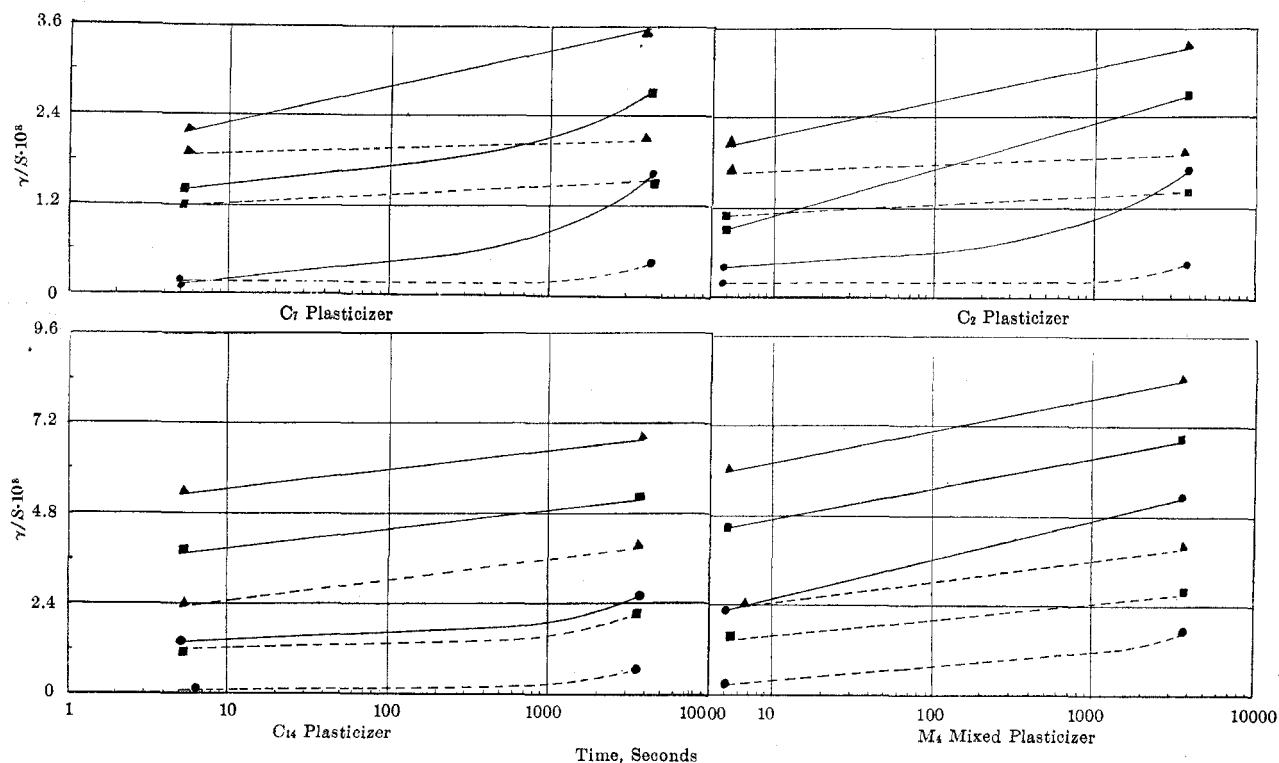


Figure 1. Creep Curves of Geon 101 Containing Liquid Polymer Plasticizer

----- 25% plasticizer

● = 10° C., ■ = 30° C., ▲ = 50° C.

—— 45% plasticizer

vinyl polymers are summarized in Tables II and III. Table II gives the properties of the liquid polymers formed from one-component monomer systems employing carbon tetrabromide as chain transfer reagent. With the exception of the first material, 2-ethyl hexyl acrylate, all the liquid polymers were compatible with polyvinyl chloride resin (Geon 101). Acrylonitrile, vinyl chloride, and vinyl acetate monomers did not yield liquid polymers under the specified polymerization conditions, and even under more favorable conditions, liquid polymer formation was not effected. Table III gives the properties of the liquid polymers prepared by copolymerization of vinyl monomers with allyl chloride. Only styrene and methacrylonitrile failed to yield satisfactory products under these conditions.

In general, the yields of the allyl liquid polymers and copolymers are less than those of the acrylates, but the former proved to be far more satisfactory as plasticizers for polyvinyl chloride. The polymerization temperature and time given in Tables II and III for preparation of the liquid polymers are identical for the various systems studied. Although each monomer system has a more optimum condition for polymerization than specified in Tables II and III, the particular reaction condition employed in this work was chosen as representative of the most general and uniform method of preparation.

The results of these investigations on liquid polymer preparation are neither conclusive nor exhaustive, and much additional work remains to be carried out to completely describe all the features. In particular, detailed studies on the composition of the liquid copolymers and the relation between plasticizing action and molecular weight may prove to be of significant interest.

CREEP BEHAVIOR OF GEON 101 PLASTICIZED WITH LIQUID POLYMERS

EXPERIMENTAL RESULTS. All the liquid polymers shown in Tables II and III were incorporated into polyvinyl chloride resin (Geon 101) for studies of tensile creep. Two of the materials, P₁ and C₁₈, appeared incompatible or partially incompatible and consequently no creep measurements were made with these.

It was apparent from the first creep studies that a diversity of plasticizing effectiveness prevailed among the various liquid polymers. The acrylate polymers and copolymers—P₂, P₁, and C₄, C₁₇, for example—had very little softening effect on the Geon 101 resin, although they did not exhibit any tendency toward limited compatibility. The liquid copolymers of vinyl chloride-allyl chloride (C₂), vinyl acetate-allyl chloride (C₇), and allyl chloride-allyl acetate (C₁₄), on the other hand, were both

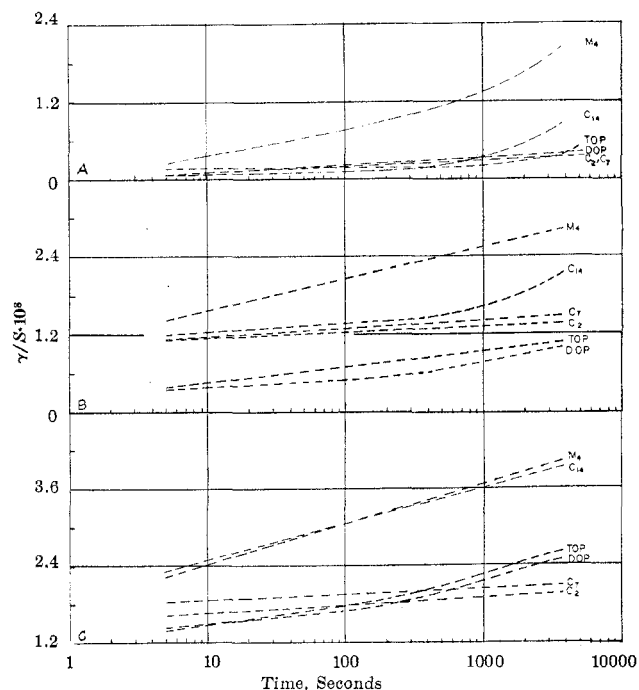


Figure 2. Comparison of Plasticizers

25% plasticizer; A = 10° C.; B = 30° C.; C = 50° C.

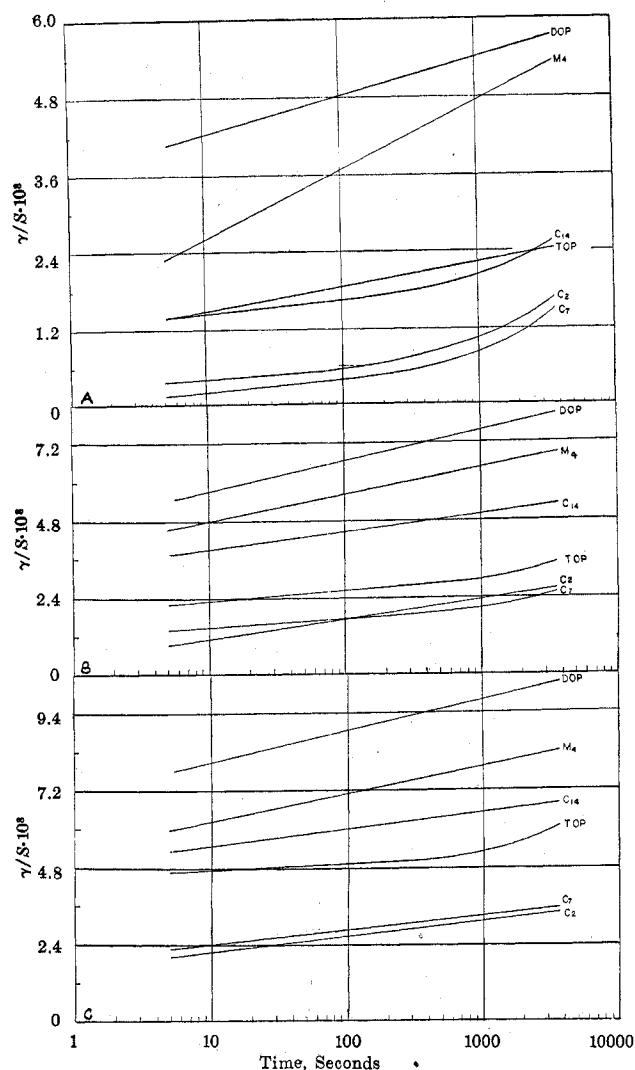


Figure 3. Comparison of Plasticizers
45% plasticizer; A = 10° C.; B = 30° C.; C = 50° C.

compatible with Geon 101 resin, based on visual examination, and brought about a pronounced softening effect. The creep behavior of films containing C₂, C₇, and C₁₄ liquid polymers was studied in detail, and the results obtained were compared with the plasticizing effectiveness of the commercial plasticizers, tri-octyl phosphate (TOP) and dioctyl phthalate (DOP). Creep studies were also made with plasticized films of VYNW resin (96 to 97% vinyl chloride, 3 to 4% vinyl acetate) but since the same, though less pronounced, trends were noted with this resin as with Geon 101, the experimental data for the former are not given.

In Figures 1, 2, and 3 are shown the creep curves of Geon 101 resin containing 25 and 45% C₇, C₂, and C₁₄ liquid polymer plasticizers at three temperatures, 10°, 30°, and 50° C. At lower temperatures (−20° C.), the compliance and extent of creep of the liquid polymer plasticized, Geon films (45% plasticizer) were so small as to be unmeasurable although the TOP and DOP films did exhibit typical creep (1) at −20° C. The curves in Figure 4 represent creep runs made on a Geon 101 film containing as plasticizer, a mixture of 70 parts by weight liquid polymer, C₇, and 30 parts DOP. (This plasticizer mixture is given the code number M₄.)

Figures 2 and 3 represent the creep data of Figure 1 plotted in a different way. At each temperature of measurement (10°, 30°, and 50° C.) the curves for all the samples containing 25%

TABLE IV. ULTIMATE TENSILE STRENGTH AND ELONGATION AT BREAK OF POLYVINYL CHLORIDE FILMS CONTAINING LIQUID POLYMER AND COMMERCIAL PLASTICIZERS

Plasticizer	Plasti- cizer, Weight %	Elonga- tion at Break ^a , %	Tensile Strength ^a , Lb./Sq. Inch X 10 ⁻³
TOP	25	465	4.1
	45	570	1.7
DOP	25	560	4.6
	45	675	1.8
TCP ^b	25	375	4.7
	45	605	1.9
C ₇	25	440	4.7
	45	670	3.7
C ₂	25	425	4.1
	45	510	3.7
C ₁₄	25	450	4.7
	45	610	3.9
M ₄	25	470	4.9
	45	575	4.6
No plasticizer	..	20	4.2

^a Average of three measurements at room temperature.

^b Tricresyl phosphate.

plasticizer (Figure 2) and 45% plasticizer (Figure 3) are represented on a single graph. Also included in Figure 2 are the creep curves for TOP and DOP films.

The elongation at break and tensile strength data of the various plasticized films are summarized in Table IV.

DISCUSSION. Figure 2 shows that at low concentration (25%) the three liquid polymers C₇, C₂, and C₁₄ are effective plasticizers, comparing favorably with TOP and DOP at the same concentration and in the temperature region 10° to 50° C. In view of the potentially low cost of producing liquid polymers, they would seem to offer some commercial promise. One unusual feature is the extremely flat character of some of the creep curves—for example, 25% C₇ and 25% C₂ at 10°, 30°, and 50° C. These films when stressed quickly undergo an elastic elongation with very little subsequent creep over a period of an hour; on removal of stress, recovery is rapid. In regard to this flat creep curve property, liquid polymers C₂ and C₇ are definitely superior to any commercial plasticizers the authors have studied.

The liquid polymers do not compare favorably with commercial plasticizers when used at a high concentration (45%). Although no evidence of limited compatibility was observed the results of tensile creep and tensile strength (Table IV) studies indicate that additional amounts of liquid polymer beyond 25% have a relatively small effect on the physical properties of the films (as compared with TOP and DOP). In this respect the liquid polymers studied were similar (1) to certain oil-type plasticizers such as PD-16. These facts suggest the possible use of liquid polymers admixed with ordinary plasticizers such as DOP and TOP. In the plasticizer mixture M₄, it was quite apparent that the inclusion of 30% DOP improved the plasticizing action considerably. The beneficial effect of employing such mixtures is also reflected in the improved low temperature creep properties wherein the liquid polymer plasticizers show up most poorly.

The ultimate tensile strength data of the plasticized films listed in Table IV show that the films containing the commercial plasticizers (TOP, DOP, TCP) exhibit a twofold or more decrease in tensile strength with increased plasticizer content (25% to 45%), whereas the corresponding changes in tensile strength for the liquid polymer plasticized films are not appreciable. This fact, considered along with the potential low cost for producing liquid polymers, suggests the possibility of their use as extenders for vinyl resins above 25% concentration.

No attempt has been made to describe here the theoretical aspects of the plasticizing action of the liquid polymers because it is felt that in order to do so, additional experiments need be

made along the following lines: First, to evaluate the μ values (5) for the liquid polymer-resin systems, and, secondly, to specify in detail the microcrystalline order of the liquid polymer plasticized polyvinyl chloride resin according to the physical methods employed in the studies of Alfrey, Wiederhorn, Stein, and Tobolsky (3). Lastly, the plasticizing action of the liquid polymers described here refers only to the systems listed in Tables II and III, and the results are not in any way representative of the plasticizing action of the various other polymeric-type plasticizers produced by industry.

ACKNOWLEDGMENT

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(Creep Behavior of Plasticized Polyvinyl Chloride)

DIPHOSPHATE ESTER PLASTICIZERS

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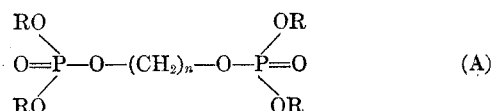
Studies on the creep behavior of vinyl chloride resin plasticized with new derivatives of phosphate esters are reported. The most satisfactory method of preparation

of a series of phosphate esters of the type $(RO)_2-P(=O)(OR)_2$

$O-(CH_2)_n-O-P(=O)(OR)_2$ was found to be reaction of stoichiometric quantities of mono- and dihydric alcohols with phosphorus oxychloride. The plasticizing efficiency of the diphosphate esters, compared by tensile creep with commercially used plasticizers, is quite satisfactory over a wide temperature range.

AMONG the widely used plasticizers for vinyl resins are the two organic ester derivatives of phosphoric acid, tricresyl phosphate (TCP) and trioctyl phosphate (TOP). Both of these materials have specific advantages and disadvantages which govern their applicability to practical use. Aside from cost factors, TOP has the distinct advantage of possessing superior low temperature properties relative to TCP and other plasticizers (1, 5). On the other hand, TOP suffers the disadvantage of high oil extractability. Several authors (1, 8) have commented on the relation between low temperature flexibility of plasticized vinyl chloride films and oil extractability of plasticizers.

In continuing the studies on polymeric plasticizers for vinyl chloride resins (3), the authors have attempted to prepare a series of phosphate esters of the type given below:



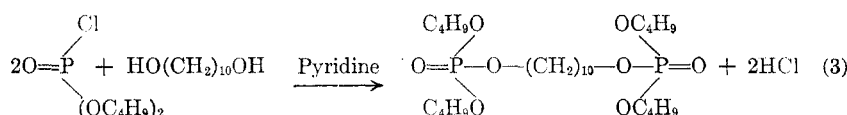
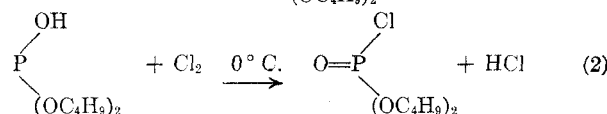
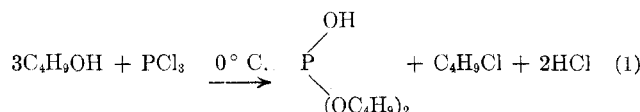
where $n = 4, 6, \text{ or } 10$, and $R = C_4H_9$, C_6H_{13} , or C_8H_{17} .

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This compound type may be considered to represent a polymeric condensation product of a phosphate ester, delimited to a degree of polymerization of two. Practical interest in these compounds arises from their potentialities as low temperature plasticizers comparable with TOP and possessing, because of their dimeric structure, oil extractability, volatile loss, and other related properties that are superior to TOP.

PREPARATION OF DIPHOSPHATE ESTERS

Preparation of *n*-decamethylenebis(*o,o*-dibutyl phosphate) was first attempted in the following way:



The dibutyl hydrogen phosphite formed in Equation 1 is converted to dibutyl chlorophosphonate by reaction with chlorine gas at ice temperature. The experimental details for the preparation of compounds similar to the phosphite and chlorophosphonate intermediates have been reported (4, 6). The final reaction product is obtained by condensation of 2 moles of dibutyl chlorophosphonate with 1 mole of decamethylene glycol (Equation 3). Pyridine is used to remove liberated hydrogen chloride. The yield by this method of preparation was low (50%) and considerable difficulty was always encountered in the purification of the reaction intermediates and the final product. Phosphite derivatives have been noted to be unstable inter-