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INTRODUCTION

The work herein reported is a part of a continuing effort on phosphate esters in which new raw materials, alternative reaction conditions, alternative refining procedures, etc. are explored in order to expand our background knowledge and maintain Monsanto's competitive position in a field in which we are well-established. This report covers the period of 1956 through mid 1957.

REFERENCES

1. Final Report on "Phosphate Plasticizers for 1954-55," Job No. 2-02-750.01-2799, March 16, 1956, by R. S. Mitchell and D. H. Chadwick.

2. Final Report on "Pilot Plant Preparation of Cyclohexyl Diphenyl Phosphate," Job No. 2-02-750.01-3067, March 21, 1956 by J. C. Goss.

3. Reports on "Exploratory Work on Phosphate Esters," Job No. 2-02-750.01-3462, by D. H. Chadwick, R. S. Mitchell and H. D. Barnstorff.

4. Final Report on "Fluid CS-70 Process Development," Job No. 2-02-750.01-3215, by R. S. Mitchell.

5. Final Report on "Minor Plant Investigations on Phosphate Ester Plasticizers 1956," Job No. 2-02-750.01-3149, Feb. 25, 1957 by R. S. Mitchell.

6. Final Report, "Exploratory Investigations, Part I, Job No. 2-02-750.01-3098, by M. W. Farrar.

7. Progress Reports, "Distillation of Esters," Job No. 2-02-750.01-2326, by R. O. Neikums and A. deAssis.

8. Final Report, "Pilot Plant Demonstration of Low Odor Santicizer 141," Job No. 2-02-750.01-3025, January 18, 1957, by J. C. Goss.

9. Progress Reports, "Phosphate Esters - Minor Plant Investigations," Job No. 2-02-750.01-3310, by R. S. Mitchell and D. H. Chadwick.

SUMMARY

A. Catalysts of reaction between cresylic acid and phosphorus oxychloride.

A variety of possible catalysts for the reaction between cresylic acid and phosphorus oxychloride were evaluated in an attempt to find a material which could be readily removed from

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the reaction mixture by filtration or distillation. Use of such a catalyst might permit refining of tricresyl phosphate by distillation. (See section D). Among the materials evaluated, Sud-Chemie acid-treated clay, born trifluoride, and titanium tetrachloride possessed appreciable catalytic activity, though none of the materials proved to be as satisfactory as aluminum chloride (the catalyst presently employed) for this reaction.

B. Catalysis of reaction between alcohols and phosphorus oxychloride

In limited earlier work at Monsanto, attempts to catalyze the reaction of alcohols with phosphorus oxychloride by aluminum chloride gave negative results. The catalytic effect of titanium tetrachloride on the reaction of phosphorus oxychloride with hydroxyaryl compounds (cresylic acid) and ethylene oxide suggested that titanium tetrachloride might catalyze the reaction between alcohols and phosphorus oxychloride. This was found to be the case.

Using titanium tetrachloride as catalyst, tri (2-ethylhexyl) phosphate was obtained in high yield with a five hour reaction time and only 10% excess alcohol, compared to a 15 to 20 hours reaction time and 170% excess of alcohol required for the uncatalyzed reaction. A patent disclosure was submitted.

C. Preparation of triaryl phosphates from phosphoryl halides by Schotten-Baumann reaction

The preparation of triaryl phosphate esters by Schotten-Baumann reaction was studied. A satisfactory yield was obtained only in the preparation from the arylphosphoryl dichloride. Lower yields were obtained in the preparations from diaryl phosphoryl monochloride and from phosphorus oxychloride. Further consideration of the Schotten-Baumann method for the preparation of triaryl phosphates is limited by the fact that at present there is no satisfactory method of preparation of aryl phosphoryl dichlorides in high yield.

D. Distillation of tricresyl phosphate

Distillation of tricresyl phosphate is a possible alternative refining process of potential value. Consideration of this method of refining is dependent upon the discovery of a catalyst which can be removed by filtration or distillation, thus permitting direct distillation of the crude condensation product. When the catalyst must be removed by aqueous washing, as is the case with the catalyst presently employed, aluminum chloride, distillation no longer offers economic advantages. Direct distillation of the aluminum chloride catalyzed crude condensate is not satisfactory. Distillation of tricresyl phosphate from catalytic amounts of [illegible] chloride or magnesium chloride resulted in [illegible] distillate (i.e. the distillate [illegible] hazy and [illegible] an equimolar complex of the halide and ester was obtained.

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In cooperation with the Pilot Plant program on the distillation of tricresyl phosphate, confirmation was obtained that total distillation of the ester does not serve as a complete replacement for permanganate refining. It can, however, serve to reduce greatly the consumption of permanganate if a lye wash is carried out after distillation and before permanganate treatment.

E. Miscellaneous preparations of tricresyl phosphate

Preparation of tricresyl phosphate by a method not requiring a catalyst was carried out by reaction of cresylic acid with phosphorus pentachloride, followed by hydrolysis to the ester. The product was obtained in lower yield than that of the standard process and with very high color.

The presence of triphenyl phosphite in the standard catalytic preparation of tricresyl phosphate did not result in a lowering of the color of the product as had been the case when phosphorus trichloride had been added to the reaction mixture.

F. Attempts to prepare cyclohexenyl phosphate esters

The suggestion was made by Drs. H. R. Gamrath and M. W. Farrar that a divinyl alkyl phosphate might be subject to controlled polymerization and could possible be prepared through Monsanto commercial alkylphosphoryl halide intermediates. Attempts to prepare 2-ethylhexyl dicyclohexenyl phosphate and butyl dicyclohexenyl phosphate by reaction of cyclohexanone with the alkyl phosphoryl halide, using pyridine as the HCl acceptor, were unsuccessful. Cyclohexanone was largely recovered and only a small amount of an apparently polymeric material was isolated.

G. Preparation of miscellaneous phosphate esters

Cyclohexyl diphenyl phosphate of satisfactory quality was prepared by the "reverse-phenate" process (preparation of the intermediate sodium phenate by addition of molten phenol to diluted caustic lye instead of the addition of lye to a phenol-water mixture) without permanganate treatment.

Butoxyethyl dicresyl phosphate was prepared for evaluation as a plasticizer which would not develop an alcohol-like odor on compounding with polyvinyl chloride. Upon milling with polyvinyl chloride, a cresol-like odor developed comparable to that developed with tricresyl phosphate.

The triaryl phosphate from Santophen 7 (benzyl phenols), the triaryl phosphate from Union Carbides coal hydrogenation product, "mixed xylenols," and an alkyl diaryl phosphate from Carbide meta-phenols 220 were prepared for evaluation as functional fluid base stocks and as plasticizers.

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H. Viscosity Stability of Fluid OS-67

A permanent increase in viscosity of the functional fluid OS-67 (a tricresyl phosphate-Aroclor formulation) was shown to occur under thermal treatment. Heating of Fluid OS-67 at 150°C. resulted in a viscosity increase, as measured in centistokes at 100°F, of 2.8, in two hours, after which the viscosity was stabilized. In Progress Report No. 5, Job No. 3215, for December 1956, similar data are given for other phosphate esters. Understanding of this phenomenon could be of value in the field of functional fluids.

CONCLUSIONS

The possibility of refining tricresyl phosphate by distillation has been of considerable interest and considerable work has been carried out in previous programs. It has now been shown that total distillation of tricresyl phosphate does not serve as a complete replacement for permanganate refining. Satisfactory stability to potassium permanganate, an important analytical property, was not obtained on the distilled ester unless the permanganate treatment was applied.

Use of distillation refining also requires use of a reactive catalyst which can be readily removed from the reaction mass by filtration or distillation. Distillation of the ester directly from the crude mixture containing the catalyst presently employed, aluminum chloride, is not satisfactory. The acid-treated clay, boron trifluoride and titanium tetrachloride, though possessing less catalytic activity than aluminum chloride, may offer solution to the problem, though considerable work would be required to develop a process employing any of these materials.

Successful catalytic preparation of a trialkyl phosphate ester was accomplished permitting synthesis of these compounds under more moderate conditions. Synthesis of trialkyl phosphates could be of potential interest.

Investigation of the Schotten-Baumann method of preparation of triaryl phosphates from phosphoryl halides showed this method to be of possible interest only in the case of preparation from an aryl phosphoryl dichloride. Consideration of this approach is limited by the fact that at the present time there is no satisfactory method of preparation of aryl phosphoryl dichlorides in high yield.

The direct synthesis of a divinyl alkyl phosphate ester was not achieved under conditions employed, the attempted reaction of cyclohexanone with alkyl phosphoryl halides, with a tertiary amine as catalyst. The synthesis of this type of material should be attempted by other methods if these compounds should become of interest.

Application of the "reverse-phenate" process, which has been used successfully in the production of 2-ethylhexyl diphenyl phosphate for over a year, can be extended to the preparation of cyclohexyl diphenyl phosphate.

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PATENT STATUS

A disclosure was made on the catalysis of the reaction between alcohols and phosphorus oxychloride.

A disclosure was submitted by Dr. Abadir and Mr. Mayberry on the catalysis of the reaction between cresylic acid and phosphorus oxychloride by the acid-treated clay.

EXPERIMENTAL WORK AND DISCUSSION

A. Evaluation of materials as catalysts for the reaction between cresylic acid and phosphorus oxychloride

A catalyst which could be removed from the reaction mixture by distillation or filtration, was sought for the reaction between cresylic acid and phosphorus oxychloride. If such a catalyst were available, refining of tricresyl phosphate by distillation might be possible (See D of this section). A number of materials were evaluated for catalytic effect by the following procedure.

The condensations were carried out by the standard laboratory procedure for the preparation of tricresyl phosphate, except that alternative compounds were substituted for the aluminum chloride, and other changes as noted. The charges (.9 mole batches) were 300 g. of cresylic acid, plasticizer grade, 138.2 g. of phosphorus oxychloride and 5.0 g. of the compound to be evaluated on the catalyst. The phosphorus oxychloride was added to the cresylic acid containing the catalyst over a period of three hours, at 65-75°C. The temperature of the reaction mixture was then raised to 135-140°C. over a three hour period and maintained at 135-140°C. for four hours. The loss in weight after this reaction sequence was employed as a measure of the catalytic effect of the material under evaluation. Non-catalytic thermal condensation will result in evolution of about one mole of HCl and catalysis by $AlCl_3$, three moles of HCl per mole of $POCl_3$. For the stated batch charge, loss of HCl would be 0.9 moles for the uncatalyzed reaction and 2.7 moles for the catalyzed reaction.

1. n-Butanol (A77320, A77348, A8C501)

Results of evaluation of the catalytic effect of n-butanol are as follows:

	Moles of HCl lost per mole of $POCl_3$
Standard Cycle	1.78
After two additional hours heating at 135-140°C.	2.08
After two more additional hours heating at 135-140°C.	2.22

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These data showed that butanol catalyzed the reaction to some extent.

In order to determine whether this catalysis by butanol was selective, the following experiment was carried out. To a charge of 188.0g. (2.00 moles) of phenol and 3.8g. of n-butanol, was added 156.4 g. (1.02 moles) of $POCl_3$ according to the standard evaluation procedure. After the standard cycle was completed, the loss in weight was equivalent to 1.24 moles of HCl. Reaction was continued under reduced pressure for five hours (max. temp. 112°C. at 35 mm.) A total loss in weight equivalent to 2.00 moles of HCl was achieved.

The reaction mixture was fractionated using a 15" by 3/4" D. glass-helices packed column. A first fraction of 59.8 g. of phenol, a second fraction of 80.9 g. (presumably phenyl phosphorodichloridate) and an undistillable oil (presumably diphenyl phosphorochloridate). The results of the fractionation showed the catalysis by butanol to be non-selective.

The data also show that the loss in weight alone is not a sufficient measure of catalytic effect. Loss in weight could also be caused by volatilization of phosphorus oxychloride. Therefore other data, such as obtained by fractionation, determination of chloride content, or actual refining to the finished ester, must be carried out in order to more accurately describe the catalytic effect of a certain material. For a quick screening test however, the weight loss can be used in preliminary evaluations as insufficient weight loss demonstrates lack of catalytic activity.

2. Triphenyl phosphite (A77317)

Triphenyl phosphite showed no catalytic effect. Loss of HCl was 0.96 moles.

3. Triethylamine (A77318)

Triethylamine exhibited little or no catalytic effect, as the weight loss was only 1.34 moles of HCl.

4. Tributyl phosphite (A77322)

Tributyl phosphite exhibited some catalytic effect. The resultant weight loss was 1.61 moles of HCl.

5. Süd-Chemie acid treated clay (A85007-8, A85014-15, A85061-63, A101259, A101269-70, A101279-80)

The catalytic effect of Sud-Chemie Acid treated clay, discovered by Dr. Abadir and Mr. Mayberry, was investigated further. Two grades of the clay were evaluated: KSF containing about 4% moisture, and K10SF anhydrous. In the following table are summarized the results of the experiments. In all batches, the catalyst was readily removed by filtration while hot before refining.

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Sud Chemie Clay Catalyst Evaluations

	1	2	3	4	5
Catalyst:	KSF	KSF	KSF (oven dried)	K10SF	K10SF
Charges:					
cresylic acid, g.	319.4	318.8	300.2	312.5	312.9
$POCl_3$, g.	138.2	138.2	18.0	18.3	18.0
Catalyst, g.	18.0	18.0	138.2	138.2	138.2
Reaction condition:	tricresyl phosphate process conditions	More severe conditions: heated to 200°C. over 6 hrs, held at 200°C. for 8 hours.	regular process conditions	After $POCl_3$ additions heated to 200°C. over 4 hours, held at 200-270°C. for 16 hours	regular process conditions
Refining conditions	Lye and water washing	Lye and water washing	Stripped off low boilers at .75 mm. to pot temp. 227°C.	Lye and water washed	Distilled
Conversion: on wt. of cresylic acid charged	72.3	67.7%	77.5%	94.1%	74.7%
Yield:	-	-	88.9%	-	88.4%

The KSF clay charge used in batch 3 had been dried in a vacuum oven, reducing the moisture content to about 2-1/2%.

The last traces of moisture were removed from the K10SF clay by azeotropic distillation with toluene.

Under rigorous reaction conditions the conversion using the clay catalyst approaches that of the standard aluminum chloride catalyzed reaction. If refining via distillation should become attractive, use of the clay catalyst could become desirable because of its ease of removal by filtration.

Under the present limitations of equipment and processing use of the clay catalyst would not be economical.

6. Polyphosphoric acid (A85018-19)

To a mixture of 150.2g. of cresylic acid and 5.1g. polyphosphoric acid was added 69.1g. (0.45 moles) of phosphorus oxychloride according to the standard cycle. The loss of HCl was 48.9 g. versus a theory loss of 49.2 g. The crude reaction mixture was given the standard tricresyl phosphate lye wash sequence, with one extra 2% lye wash required to remove partial esters. It was then water washed to neutrality, dehydrated, and filtered, yielding 73.5 g. of tricresyl phosphate. This represented a weight yield of 52.5%, based on weight of cresylic acid charged.

Polyphosphoric acid demonstrated some catalytic effect on the reaction but not to a sufficient extent to be acceptable.

7. Toluenesulfonic acid (A85027)

Using the standard charges, except that 9.0 g. of toluenesulfonic acid was used, a loss of 1.90 mole of HCl occurred. The toluenesulfonic acid partially catalyzed the reaction, but not to sufficient extent to be practical.

8. Boron Trifluoride (A94655-57, A-1252-53,

To a standard charge of cresylic acid and 13.0 g. of boron trifluoride phenol complex, a standard charge of $POCl_3$ was added. After addition of the $POCl_3$ was completed, an additional 3.0 g. of boron trifluoride (as the complex) was added and the regular heating cycle carried out. The loss of HCl was 2.11 moles.

The crude reaction mixture was fractionated, using a 12" glass helices packed column. A cresylic acid fraction of 55.2g. (b.p. 75-97°C., 22 mm.) and a 12.5 g. fraction (b.p. 75-90°C., 1.8 mm. and pot temp. of 240°C.) were obtained. The ester could not be distilled through this column at pot temp. of 240°C., 1.8 mm.

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The ester was refined by the regular washing procedure, with three extra 2% lye washes required, giving 236.8 g. of product. This is a yield of 78.9 weight percent, based on cresylic acid charged, and 96.3 wt. %, correcting for recovered cresylic acid. Catalysis of the reaction between cresylic acid and phosphorus oxychloride by boron trifluoride is shown to be promising by this experiment.

A second experiment employing boron trifluoride as catalyst was made, using more rigorous condition than those of the first experiment. A charge of 310.0 g. of distilled cresylic acid, 15.6 g. of boron trifluoride ether complex, and 138.2 g. of phosphorus oxychloride was used. After addition of the $POCl_3$ to the cresylic acid-BF_3 mixture was completed under standard conditions, the reaction mass was heated to 200°C. over a 4-1/2 hour period and maintained at 200°C. for twelve hours. The resultant crude product was subjected to straight take over distillation. A cresylic acid fraction, 30.8 g. (b.p. 125-130°C, 38-47 mm) an arylphosphoryl halide fraction, 17.3 g. (b.p. 78-105°C, 0.6 mm), a main fraction 226.9 g. (b.p. 178-213°C. 0.6 mm) and a residue of 15.2 g. were obtained. This represents a yield of 84%, based on phosphorus oxychloride and 91% on unrecovered cresylic acid.

The main fraction was found to be acidic and contained partial esters, requiring two washes with 300 ml. portions of water containing 5 ml. of plant lye. After a negative partial ester test was obtained, the ester was washed neutral and given the potassium permanganate treatment for four hours at 55-60°C. A total of 58.9g. of $KMnO_4$ were required, an extremely high amount. After finishing the refining the ester was still very yellow colored with an acidity of .30 meq/100g.

Though under the conditions of this experiment, satisfactory ester was not obtained, it is possible that fractionation instead of take-over distillation might give a product which could process satisfactorily.

9. Tributyl borate (A-4694-90)

Using the standard charges of cresylic acid and phosphorus oxychloride and 9.0 g. of tributyl borate as possible catalyst, reaction was attempted under standard conditions with a loss a HCl of 1.90 moles (versus a theory loss of 2.70 moles) incurred.

The reaction mixture was fractionated using a 18" glass helices packed column, yielding 64 g. of unreacted cresylic acid essentially no cresyl phosphoryl dichloride, 115 g. of dicresyl phosphoryl monochloride, and 149 g. of crude tricresyl phosphate. This initial experiment indicates the possibility that tributyl borate, under proper selected reaction conditions, could catalyze the reaction more completely to either the monochloride intermediate or to the tertiary ester.

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10. Phosphorus pentachloride (A96219)

Phosphorus pentachloride was evaluated as a possible catalyst, using 9.2 g. of the PCl_5, 310.1 g. of cresylic acid and 138.2 g. of $POCl_3$, according to the standard conditions. The loss of HCl was only 1.43 moles versus the theory loss of 2.70 moles showing that the PCl_5 had essentially no catalytic effect on the reaction.

11. Titanium tetrachloride (A96223, A96227-28)

Titanium tetrachloride was evaluated for catalytic effect, using charges of 155.3 g. of cresylic acid, 69.1 g. of $POCl_3$ and 4.6 g. of $TiCl_4$. Upon mixing the titanium tetrachloride with the cresylic acid, a blood-red complex formed immediately, with only very little rise in temperature. Reaction with $POCl_3$ was carried out under the standard conditions, resulting in a loss of 1.20 moles of HCl versus a theory loss of 1.35 moles. Catalysis by titanium tetrachloride was therefore indicated.

The crude reaction mixture was given three lye washes under the conditions of the standard process for the refining of tricresyl phosphate, two water washes, two acid washes, each containing 20 ml. of HCl, six water washes, a lye wash and four final water washes. All washes were about 200 ml. each and at 55-60°C. Upon dehydration and filtration, 148.7 g. of ester was obtained, representing a 95.8 weight percent yield based on $POCl_3$. The ester was very dark colored with an acidity of 3.5 MM.

While titanium tetrachloride catalyzes the reaction between cresylic acid and phosphorus oxychloride, the quality of the ester so produced was far from satisfactory and could not be brought to specification quality by simple washing procedures.

The preparation of the ester was repeated and refining by distillation was attempted. The distillate was blood-red in color, as colored as the crude ester before distillation. The titanium tetrachloride apparently distilled over and complexed with the distillate. It is possible that a satisfactory technique can be developed for the removal of titanium tetrachloride since successful removal of this catalyst from trialkyl phosphate preparations was accomplished.

B. Catalysis of reaction between alcohols and phosphorus oxychloride

Successful catalysis of the reaction between alcohols and phosphorus oxychloride has not been reported. Aluminum chloride has been tried with little success (Monsanto Report No. 53, Job No. 117-1799) and magnesium chloride is indicated to have some effect (British Patent 734,768). Phosphorus trichloride is reported to catalyze the partial esterification of phosphorus oxychloride with ethylene oxide or alcohols (U.S. 2,716,657). The reaction between

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ethylene oxide and phosphorus oxychloride is also reported to be catalyzed by aluminum chloride (Monsanto Report, Job No. 117-2136) and by titanium tetrachloride (U.S. 2,610, 978).

Catalysis of the reaction would make the preparation of trialkyl phosphates more attractive economically. Non-catalytic preparation of a trialkyl phosphate involves the use of an extremely large excess of the alcohol and lengthy time cycles. It was decided therefore, to investigate this problem briefly.

1. Evaluation of titanium tetrachloride (A96233-36, A96238, A96240-41)

Titanium tetrachloride was evaluated for possible catalytic effect in the preparation of tri 2-ethylhexyl phosphate. The charge consisted of 214.8g. (1.65 moles, a 10% excess) of 2-ethylhexanol, 6.6 g. of titanium tetrachloride, and 76.7 g. (0.50 moles) of phosphorus oxychloride. Upon addition of the $TiCl_4$ to the 2-ethylhexanol, the mixture turned yellow and temperature rose from about 25°C. to 32°C.

The $POCl_3$ was added dropwise at 5-15°C. over about an hour. The cooling bath was removed and the mixture allowed to come to room temperature over about a period of about one hour. Pressure was then gradually reduced to about 25 mm and maintained at this pressure about 1-1/2 hours. The reaction mixture was then heated to reflux (95-105°C.) and kept at the stated temperature and pressure for two hours. The loss in weight was 58.5 g., 1.58 moles as HCl.

The reaction mixture was washed twice with 250 ml. H_2O containing 10 ml. of HCl, at room temperature, for about 1/2 hour each, followed by five water washes of 250 ml. and 5 minutes each. Stripping, at atmospheric pressure was conducted until about 500 ml. distillate was collected. From the distillate 20 ml. of 2-ethylhexanol were recovered. The ester was dehydrated and filtered through Dicalite Speedplus, yielding 212.7 g. of tri 2-ethylhexyl phosphate, a yield of 97.8% based on $POCl_3$. The ester was hazy with acidity 2.5 MN, indicating incomplete washing and removal of titanium compounds. (Subsequent work, on Job No. 3-62, established a satisfactory washing procedure.) The specific gravity, 0.922/25°C. and n_D^{25}, 1.4425 compare very well with the values, 0.9225-0.9235 and 1.4420, respectively, for Union Carbides product, ("Plasticizer TOP").

The preparation of tri-isooctyl phosphate, from the oxo process iso-octanol was demonstrated also.

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As a control, the reaction sequence was carried out with 2-ethylhexanol and $POCl_3$, without a catalyst. Under these conditions, the reaction did not proceed satisfactorily and resulted largely in formation of partial esters.

Catalysis of the reaction between alcohols and phosphorus oxychloride thus was demonstrated. A patent disclosure, No. 1942, was submitted.

Further work as this subject was carried on under Job No. 2-02-750.01-3462.

2. Evaluation of tributyl borate (A96239)

Tributyl borate was evaluated for catalytic effect on the reaction by the attempted preparation of tri 2-ethylhexyl phosphate according to the reaction sequence of the previous sub-section using 7.3 g. of tributyl borate. Catalytic effect was not observed as partial esters were obtained principally.

C. Preparation of triaryl phosphates from phosphoryl halides by Schotten-Baumann reaction

In earlier work, yields of tricresyl phosphate of 75-80%, based on $POCl_3$, were obtained in its preparation from $POCl_3$ by Schotten-Baumann reaction using the conditions of the Santicizer 141 process. The Santicizer 141 (2-ethylhexyl diphenyl phosphate) yield is about 90-91% and that of tricresyl phosphate by the standard catalytic condensation process is about 94% based on $POCl_3$. Therefore it was decided to modify the preparation of a triaryl phosphate via Schotten-Baumann reaction by reacting sodium cresylate with phenyl phosphoryl chlorides in order to determine whether a yield could be obtained comparable to that of the standard catalytic condensation process.

1. From phenyl phosphoryl dichloride (A94697-98, A96209-10)

Exp. 1. One mole of re-distilled phenyl phosphoryl dichloride was reacted at 10-15°C. with 2.12 moles of sodium cresylate under conditions similar to those used in the preparation of Santicizer 141 (2-ethylhexyl diphenyl phosphate) from 2-ethylhexyl phosphoryl dichloride and sodium phenate. After a lye and water washing sequence similar to that of the tricresyl phosphate process, the ester was dehydrated and filtered, yielding 323 g. of dicresyl phenyl phosphate, an 89.3% yield, based on phenyl phosphoryl dichloride and assuming the molecular weight of cresylic acid to be 112. This yield justified further study of this method of preparation of phosphate esters.

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Exp. 2. This reaction was repeated, carrying out the Schotten-Baumann reaction at a lower temperature, about -10°C. All other steps were unchanged. The ester was obtained in 90.1% yield, an increase of about 1%.

2. From diphenyl phosphoryl monochloride (A96215-16)

A sample of diphenyl phosphoryl monochloride which had been prepared by Samuel Kaufman was redistilled. A charge of 134.5g. (0.50 moles) of the purified material was reacted with 0.54 moles of sodium cresylate at 5-10°C. After completion of the Schotten-Baumann reaction, refining was carried out in the same manner as the previous experiments. A yield of 142.1g. of cresyl diphenyl phosphate, 82.6% based on diphenyl phosphoryl chloride, was obtained. This lower yield obtained when the diaryl phosphoryl monochloride was employed is attributed to lower solubility of the monochloride in the reaction medium. In order to determine if addition of a solubilizing agent would increase the yield, the following experiment was done.

3. From phosphorus oxychloride in tricresyl phosphate solution (A96217-15)

A charge of 138.3 g. (0.90 mole) of $POCl_3$ was dissolved in 300.3g. of tricresyl phosphate. Reaction was carried out with 2.77 moles of sodium cresylate at 5-15°C, with the portionwise addition of 352.4 g. of plant lye being required in the latter stages of the reaction in order to maintain alkalinity. After the regular sequence of refining, the ester was obtained in 73.0% yield, corrected for the tricresyl phosphate charge in the $POCl_3$ and based on $POCl_3$. This yield is quite similar to that obtained in previous Schotten-Baumann preparations of tricresyl phosphate from phosphorus oxychloride. There was no improvement by this approach.

4. From reaction mixture of 1 mole of $POCl_3$ and 1 mole of cresylic acid (A96212-13)

The possibility of replacing the purified aryl phosphoryl chlorides with the crude reaction product from 1 mole of $POCl_3$ and 1 mole of cresylic in the Schotten-Baumann reaction was investigated.

From a dropping funnel, 153.4 g. of $POCl_3$ (1.0 mole) was added to 112.1 g. (1.0 moles) of cresylic acid at 70-80°C. over 1-1/2 hours. The reaction mixture was then heated to 130-135°C. over about 1/2 hour and maintained at this temperature for 4-1/2 hrs. Though after this reaction cycle, only 5.3g. weight loss was obtained, the mixture was reacted with 2.11 moles of sodium cresylate at 10-15°C. An extra 102.6 g. of plant lye was required during the reaction in order to maintain alkalinity. After the usual refining, only 233.3 g., a 61.4% yield, based on $POCl_3$, was obtained. Thus this method is not satisfactory for the preparation of triaryl phosphates.

DSW 621351

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Further consideration of the Schotten-Baumann method for the preparation of triaryl phosphates is limited by the fact that at present there is no satisfactory method of preparation of specific aryl phosphoryl chlorides in high yield. Thus, though a satisfactory yield was obtained in the preparation from phenyl phosphoryl dichloride, the difficulty of preparation of the halide precludes further consideration of this approach at this time.

5. Preparation of sodium cresylate by "reverse" method in presence of charcoal (A96211)

The possibility of preparing colorless sodium cresylate by reverse addition of reactants (cresylic acid addition to lye solution) in the presence of charcoal was investigated. To a mixture of 87.2 g. of plant lye, 1.2 g. Norit A in 140 ml. H_2O, [illegible].7 g. of distilled plasticizer grade cresylic acid was added, maintaining temperature between 5-15°C. After reaction was completed, the batch was filtered through Attapalgus Earth. The filtrate was highly colored. Using commercial cresylic acid, a colorless sodium cresylate solution can't be prepared by this approach.

D. Distillation of tricresyl phosphate (A96208, A96214)

1. Distillation from catalysts

Preliminary experiments on the distillation of tricresyl phosphate were carried out to evaluate the possibility of refining the ester by distillation. Distillation of the ester from over catalysts was undertaken.

a. Control distillation

Using straight take-over apparatus a charge of 102.2g. of tricresyl phosphate, A grade, was distilled. The ester distilled cleanly at 220-240°C. and 0.75 mm, yielding 99.5 g. of essentially colorless distillate. There was no carbonization of the residue (2.7g).

b. Distillation from aluminum chloride

Three grams of $AlCl_3$ were added to 101.2 g. of tricresyl phosphate, A grade, and the mixture subjected to straight take-over distillation. On heating the mixture, the ester darkened very rapidly with vigorous evolution of gas. Until evolution of gas ceased, the pressure could not be reduced to the desired level. At 0.7 - 0.9 mm. the ester distilled at 235-265°C, the distillate being yellow-orange in color. A black, tarry residue, 11.8 g., was obtained.

DSW 621352

STLCOPCB4095382

c. Distillation from magnesium chloride

Two and a half grams of anhydrous magnesium chloride was added to about 100 g. of tricresyl phosphate, A grade. Straight take-over distillation at 220-260°C. and 0.3 - 0.4 mm. yielded a hazy slightly yellow product. Again, about 11 g. of residue were obtained.

In both distillations from over catalysts quality of the ester was affected and an amount of residue equivalent to an equimolar complex of the metal halide and the ester resulted.

2. Stability to potassium permanganate of tricresyl phosphate distilled in pilot plant (A96202)

The stability to potassium permanganate of sample of tricresyl phosphate distilled in the pilot plant was determined (See Reference 7 for details of the distillation).

The stability of Batch 1 was 31% (65% specification minimum). Then 98.8 g. of the distilled ester from Batch 3 were subjected to the $KMnO_4$ treatment for three hours at 50-60°C, with 2.8 g. of $KMnO_4$ required. The stability to potassium permanganate of the finished treated ester was 83%, a satisfactory value.

A sample, 101.3 g. of pilot plant Batch 1 distilled ester was given a 1% lye wash at 20°C, water washed to neutral (1 washes required) and given the $KMnO_4$ treatment for one hour, only 0.2 g. of $KMnO_4$ being required. The stability of the finished ester was 91%.

These data confirm previous work on the distillation of tricresyl phosphate in the Pilot Plant in which it was shown that the total distillate product, though of specification color, possessed poor stability to potassium permanganate. Although total distillation of tricresyl phosphate does not serve as a complete replacement for permanganate refining, it can serve to reduce greatly the consumption of permanganate if a lye wash is carried out after distillation and before permanganate treatment.

These data are in accordance with information as to the probable procedure used by the Celanese Corporation for the manufacture of triaryl phosphates.

On the basis of an article in "Chemical Week", Oct 13, 1956, p. 67 this process appears to consist of thermal condensation, distillation, followed by aqueous permanganate refining.

DSW 621353

STLCOPCB4095383

E. Miscellaneous preparations of tricresyl phosphate

1. In presence of triphenyl phosphite in the cresylic acid (A96220)

Previous work had shown that the preparation of tricresyl phosphate from phosphorus oxychloride containing about 5% phosphorus trichloride resulted in a significant lowering of the color of the ester. Since this process had been patented by Metallgesellschaft AG, Germany, (U.S. 2,716,657), the effect of the presence of a phosphite ester in the condensation step on the color of tricresyl phosphate was determined.

A standard laboratory batch of tricresyl phosphate was prepared, except that 15.5 g. of triphenyl phosphite representing 5% by wt. of the cresylic acid charge of 310 g. was dissolved in the cresylic acid. After refining by lye and water washing, the ester was obtained with no reduction in color from that of regular non-permanganate treated material.

2. From phosphorus pentachloride (A96221-22)

Preparation of tricresyl phosphate from phosphorus pentachloride was carried out. To 154.8 g. (1.38 mole) of cresylic acid, 93.7 g. (0.45 mole) of phosphorus pentachloride was added portionwise at 70-90°C. over 1/2 hour. The reaction mixture was heated to 135°C. over a three-hour period and maintained at 135-140°C for four hours. A loss in weight of 42.7 g. versus a theory loss of 49.3 g. of HCl was obtained.

Then 380 ml. of water was carefully added to the crude product, with considerable evolution of heat and HCl. To this, 30 ml. of plant lye was added and the mixture stirred for 1/2 hour. This was followed by a 3% and two 2% lye washes according to the condition of the regular tricresyl phosphate process. After water washing and dehydration, 130.6 g. of product was obtained, an 84.5% weight yield based on cresylic acid. This yield is about 20% lower than that of the regular preparation from phosphorus oxychloride. This fact, and the very high color, about NPA 4 to 5 do not make this procedure attractive.

3. Attempted removal of catalyst by calcium hydroxide (A85016-17)

An attempt was made to convert the catalyst of the tricresyl phosphate process into a filterable form by neutralization with $Ca(OH)_2$. Aluminum chloride is successfully removed from the crude reaction product of the isopropyl biphenyl process by such means. (See U.S. 2,734,892). Removal of the aluminum chloride from the crude tricresyl phosphate reaction product by filtration might permit refining of the ester by distillation. As shown by preceding experiments, tricresyl phosphate cannot be distilled satisfactorily in the presence of aluminum chloride.

DSW 621354

STLCOPCB4095384

A standard 0.9 mole laboratory batch of tricresyl phosphate was condensed. After condensation was completed, the crude reaction product was heated briefly to 200°C. under reduced pressure, 34 mm. Nothing could be distilled from the batch under these conditions. The batch was restored to atmospheric pressure, cooled to 80° - 85°C. The 23.7 g. of $Ca(OH)_2$ and 13 ml. H_2O (the ratio employed in the isopropyl biphenyl process) were added, the temperature rising quickly to 98°C. The mixture was cooled to 75-85°C and maintained there for thirty minutes. Filtration was attempted through Dicalite Speedplus without success. The mass set-up nearly solid and was not filterable.

F. Attempts to prepare cyclohexenyl phosphate esters

In exploratory experiments by Dr. M. W. Farrar, a small amount of a product analyzing essentially correctly for tricyclohexenyl phosphate was obtained. This material polymerized very readily. It was suggested by Dr. H. R. Gamrath and Dr. M. W. Farrar that a divinyl alkyl phosphate might be less subject to uncontrolled polymerization and could possible be prepared through the Monsanto commercial alkylphosphoryl halide intermediates.

1. Attempted preparation of butyl dicyclohexenyl phosphate (AP5203-04)

Butyl phosphoryl dichloride was prepared according to the standard procedure for the preparation of the intermediate 2-ethylhexyl phosphoryl dichloride of the Santicizer 141 process.

A mixture of 68.2 g. (0.70 moles) of cyclohexanone and an excess, 67.4 (0.85 moles) of pyridine was dissolved in 150 ml. of benzene in a 500 ml. 3-necked o flask and cooled to 15°C. From a dropping funnel 53.3 g. (0.33 moles) of butyl phosphoryl dichloride was added, keeping the temperature between 15 - 20°C.

During the addition, which required about 3/4 hour, the mixture became cloudy. The mixture was allowed to stir at room temperature over night during which time the precipitated material became light tan. It was next heated to reflux and maintained at about 90°C. for four hours resulting in solution of the precipitate. After cooling to room temperature, 150 ml. of water was added, with no rise in temperature observed. Two more water washes were given and the organic layer dried overnight over $MgSO_4$. The solvent was removed under vacuum leaving a small amount of an oil which was subjected to distillation. Only 10.8 g. distillate was obtained, leaving 8.7 g. of residue. Refractive index of the distillate indicated it to be cyclohexanone. Therefore essentially none of the desired ester was made by this procedure.

DSW 621355

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2. Attempted preparation of 2-ethylhexyl dicyclohexenyl phosphate (A96205)

Using the same charges of cyclohexanone, pyridine, and benzene as in the previous experiment, reaction was attempted with 71.3 g. (0.33 moles) 2-ethylhexyl phosphoryl dichloride at 15-20°C. After addition was completed, the mixture was stirred at room temperature overnight. The mixture was filtered, giving a filter cake of 52.9 g. The filtrate was warmed to 32°C. for two hours with no evidence of further formation of a precipitate. The material was then subjected to straight take-over distillation. In addition to the solvent, the only distillate collected was a mixture of cyclohexanone and pyridine. Only 23.9 of residue remained as an apparently polymerized material. The desired product was not obtained.

3. Attempted preparation of tricyclohexenyl phosphate (A96206-07)

The preparation of tricyclohexenyl phosphate according to the conditions reported by Dr. Farrar was attempted. Into 150 ml. benzene were mixed 98.1 g. (1.0 moles) of cyclohexanone and 95.0 g. (1.20 moles) of pyridine. By dropping funnel, 51.1 g. (0.33 moles) of phosphorus oxychloride was added over about 3/4 hour at 15-21°C. The mixture was then heated to about 90°C. and maintained at this temperature for about 8 hours and then allowed to stand overnight at room temperature. A dark brown precipitate settled out, which dissolved when 150 ml. of water was added to the mixture, the temperature using to 34°C. Three 250 ml. water washes were given and the organic layer dried overnight over $MgSO_4$. The dried organic layer, yellow-orange in color, was freed of solvent and cyclohexanone under vacuum, giving 26.4 g. of an oil.

Flash distillation of this oil was attempted. The oil was slowly dropped into a flask heated to about 275-280°C. at 0.9 mm. Below this temperature, no distillation occurred. Even at the higher temperatures, the material did not flash-off, but polymerized. The desired product was not isolated.

Another approach to the preparation of these desired compounds should be carried out in order to obtain material for evaluation as possible polymerizable plasticizers.

G. Miscellaneous preparations

1. Cyclohexyl diphenyl phosphate via "reverse-phenate" process (A94667, A94675)

Verification was needed that the permanganate treatment could be eliminated from the preparation of cyclohexyl diphenyl phosphate, when prepared by the "reverse-phenate" process. It had been proved previously that Santicizer 141 (2-ethylhexyl diphenyl phosphate) of specification color could be produced without permanganate treatment when the intermediate sodium phenate was prepared by the (reverse) addition of molten phenol to diluted plant lye instead of the addition of plant lye to a phenol-water mixture.

DSW 621356

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This process change had been successfully employed in the production of Santicizer 141 for several months.

From a batch of cyclohexyl diphenyl phosphate prepared in the Pilot Plant, using "reverse-phenate" process, a sample was taken after the post-steaming wash sequence (before $KMnO_4$ treatment) and dehydrated in the laboratory. The dry ester was treated for 1/2 hour with charcoal (Norit A) at about 50°C. Analysis of this finished ester is as follows, in comparison with the analysis of finished material from the Pilot Plant which was given permanganate treatment:

	No $KMnO_4$ treatment	$KMnO_4$ treated
Ref Index 25°C	1.5338	1.5340
Moisture	0.13%	0.09%
Sp. Gr. 25/25°C.	1.1752	1.1763
Color	APHA 20	APHA 20
Acidity	0.12 meq/100 g.	0.07 NN

The same color was achieved without the permanganate treatment as with it.

Later about 200 pounds of cyclohexyl diphenyl phosphate were prepared in the Pilot Plant using the "reverse-phenate" process. An in-process sample was taken after the post-steaming lye wash and finished in the laboratory by washing with water until neutral (nine washes required), dehydration under vacuum, and filtration through Dicalite Speedplus. Color of the finished ester was APHA 100. The ester was stirred for 1/2 hour with charcoal (Norit A) at 45-55°C. and filtered through Attapulgus Earth. Color of the ester was reduced to APHA 20.

Cyclohexyl diphenyl phosphate of low color can be prepared without permanganate treatment using the "reverse-phenate" process by simple treatment with charcoal.

2. Butoxyethyl dicresyl phosphate (A94689-91)

Deodorized Santicizer 141 tends to redevelop odor when compounded with polyvinyl chloride. An additional market has been predicted for a similar product which would not redevelop odor on compounding. The limited data available suggested that butoxyethyl dicresyl phosphate could be such a product. A one mole batch was made according to the charge ratios and conditions of the Santicizer 141 process, including the "reverse-phenate" modification. A treatment with charcoal (Norit A) was included. The product was obtained in 82% yield, based on phosphoric oxychloride, with acidity of 0.10 meq./100 g. and with quite high color, APHA 400.

DSW 621357

STLCOPCB4095387

Upon milling with polyvinyl chloride a cresol-like odor developed, comparable to that developed when tricresyl phosphate is employed as the plasticizer. This difference from the alcohol-like odor developed when Santicizer 141 is employed suggests that further work along this line could be worthwhile.

Interest soon re-developed in deodorized Santicizer 141 because of modification of processing conditions for certain applications by customers. Extensive work was then carried out in the Pilot Plant and Interim Production Facilities on vacuum-steaming of the ester. (See References 8,9) which led to the decision to incorporate vacuum-steaming into the Sant. 141 process. A Girdler deodorizer became available from the idle Monsanto plant at Norfolk, Virginia, about this time and was transferred to the J. F. Queeny Plant for installation in late 1957 and early 1958.

3. Tri benzylphenyl phosphate from Santophen 7. (A96232)

Tri benzylphenyl phosphate was prepared from Santophen 7 (a benzylphenol mixture).

Using the following charges,

Santophen 7,	140.8 g.	(0.75 moles)
$POCl_3$	38.3 g.	(0.25 moles)
$AlCl_3$	4.2 g.	

the ester was prepared according to the conditions of the tricresyl phosphate process, with the refining steps shortened to lye and water washing. A yield of finished ester of 132.9 g., 89.1% of theory based on $POCl_3$ resulted.

The ester, a clear viscous liquid was submitted for evaluation as functional fluid. Viscosity data are as follows:

Viscosity	
KV 100°F	681.6 cs.
KV 210°F	18.47 cs.
Viscosity Index	- 80

DSW 621358

STLCOPCB4095388

4. Triaryl phosphate from "Mixed Xylenols." (A85419-21)

A sample of "Mixed Xylenols," a coal-hydrogenation product of Union Carbide, was obtained. Analysis of the material is as follows:

Dist Range	
1st drop	199.7°C
1% off	216.0
10% off	217.2
25%	218.2
50%	220.2
70%	223.0
90%	231.8
95%	236.3
Dry Point	244.4
Appearance	dark amber liquid
Ortho-cresol	4.13%
Moisture	0.8%
Oil and naphthalene	0.4%
Sp. Gr. 25/25°C	1.0133

A sample of the material was distilled and converted to the phosphate ester according to the conditions of the tricresyl phosphate process, charging 360 g. of "mixed xylenols, 10 g. of $AlCl_3$, and 138.2 g. of $POCl_3$. Refining consisted of standard lye washing, water washing, dehydration and filtration. There were obtained 318.2 g. of product, an 88.4 wt. percent yield, based on weight of xylenols charged.

The finished ester was submitted for evaluation as a functional fluid base stock. Analysis is as follows:

Acidity	0.18 meq./100 g.
Sp. Gr. 25/25°C.	1.1284
Ref. Index 25°C.	1.5486
Viscosity	
KV, 100°F	41.34 cs.
KV, 210°F	5.06 cs.
Viscosity Index	117

DSW 621359

STLCOPCB4095389

There was no further interest in this material after the discontinuance of the coal-hydrogenation product by Carbide and Carbon.

5. Alkyl diaryl phosphate from meta-phenols 220 by "reverse-phenate" procedure (A85020-22)

The use of "meta-phenols 220," a coal-hydrogenation product of Union Carbide in the preparation of triaryl phosphate esters has been reported previously.

The preparation of an alkyl diaryl phosphate ester of the Santicizer 141 type from meta-phenols 220 was carried out. Assuming a molecular weight of 125 for meta-phenols 220, the following charges were used:

meta phenols 220	265 g (2.12 mole)
Plant lye (47.8%)	177.7 g. (2.12 moles, as NaOH)
2-ethylhexyl phosphoryl dichloride	247.1 g. (1.00 moles)

The reaction was carried out according to the standard process for the production of Santicizer 141, employing the reverse phenate modification.

The color of the intermediate sodium salt was quite high (orange) even though the reverse method of addition was employed. This intermediate was then reacted with 2-ethylhexyl phosphoryl dichloride obtained from Dept. 50 of the J. F. Queeny Plant. During this reaction, additional lye was required in order to maintain alkalinity. After the standard lye washing, an extra lye wash was required because of the presence of partial esters. After finishing the refining by water washing to neutral (twelve washes required) dehydration and filtration, the ester was obtained in 79.2% yield, 335.8g., based on the octyl phosphoryl dichloride. Acidity was 0.30 meq/100 g. and the color, bright yellow.

Meta-phenols 220 was unsatisfactory for the preparation of a low-color alkyl diaryl phosphate ester for plasticizer use by the Santicizer 141 process. Though this ester might be of use in the field of functional fluids, the withdrawal of meta-phenols 220 from the market by Carbide and Carbon cancelled further work on its use.

DSW 621360

STLCOPCB4095390

H. Viscosity Stability of Fluid OS-67 (A91687-88)

On Job No. 3215, the effect of heating on the viscosity stability of certain phosphate esters is discussed. In summation, it was found that the viscosity of these esters, as measured in centistokes at 100°F, increases upon exposure to heat and reaches a point after which no further viscosity increase occurs. Similar data were determined for Fluid OS-67, a phosphate ester-Aroclor blend.

A sample of Fluid OS-67 in a r.b. flask was heated at 150°C with gentle stirring over 50 hours. Sample were withdrawn periodically and the viscosity determined. Data are summarized as follows:

	Time of heating, hours				
	0	2	4	8	50
Viscosity, cs.					
@ 210 °F	4.93				5.00
@ 100°F	84.0	86.3	86.3	86.6	86.4
Viscosity Index	-358				-349

These data show a permanent increase in viscosity of the fluid: a viscosity increase of 2.8%, as measured in centistokes at 100°F, after two hours heating at 150°C, after which the viscosity was stabilized. Understanding of this phenomenon could be of value in the field of functional fluids.

For further work on this subject see the reports on Job Numbers 3215 and 3462.

RECOMMENDATIONS FOR FUTURE WORK

If further work as the distillation of tricresyl phosphate should make this method of refining attractive, enlarged study of the use of the acid-treated clay catalyst, boron trifluoride, and titanium tetrachloride is suggested.

The catalytic preparation of trialkyl phosphates will be investigated further. Other possible catalysts will be sought and scope of the catalysis, such as possible extension to preparation of dialkyl phosphoryl chlorides (for dialkyl aryl phosphates) will be

Another approach to the preparation of vinyl alkyl phosphates should be carried out in order to obtain material for evaluation as possible polymerizable plasticizers.

DSW 621361

STLCOPCB4095391

ANALYTICAL PROCEDURES AND MATERIAL SPECIFICATIONS

A. Analytical Procedures

The raw materials and products were analyzed by standard well-known methods.

B. Raw Material Specifications

Those chemicals used which are standard raw materials in the J. F. Queeny plant must meet the specifications established for these materials.

C. Finished Goods Specifications

Specifications for tricresyl phosphate are readily available and will not be repeated here.

TOXICITY AND HAZARDS

Care should be taken in the handling of such corrosive and dangerous materials as phosphorus oxychloride, cresylic acid, aluminum chloride, potassium permanganate, sulfuric acid, and sodium hydroxide.

The toxicological properties of tricresyl phosphate are known to be directly related to the ortho-cresol content of the cresylic acid used. Therefore care should be used in the handling of the ester prepared from a cresylic acid of higher ortho-cresol content than that of regular plasticizer grade cresylic acid (3% ortho-cresol maximum)

APPENDIX

Notebook Pages: RSM

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	A 77322		A 96232-36
	A 77348		A 96238-41
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5/8/58

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