

The Determination of *o*-Tolyl Ester in Tritolyl Phosphate

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A method has been devised for the determination of the *o*-tolyl ester in commercial tritolyl phosphate. The test, which is based on previous work carried out by Wurzschnitt, involves the preliminary isolation of the mixed cresols from the ester, followed by condensation of these cresols with benzaldehyde in a sulphuric acid medium. On being made alkaline the product obtained from *o*-cresol under these conditions yields a coloured solution, which is examined absorptiometrically. The method is suitable for the determination of up to 6 per cent. of *o*-tolyl ester in commercial tritolyl phosphate, without modification, and of a corresponding amount of *o*-cresol in mixed cresols. The influence of phenol and various xylenols on the test has been investigated.

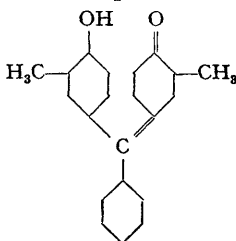
CONSIDERABLE interest has been taken recently in this country in the proportion of *o*-tolyl esters in commercial samples of tritolyl phosphate. The reason for this is that there appears to be no doubt that tri-*o*-tolyl phosphate is a dangerously toxic material. There is a voluminous literature on the subject and Blomqvist¹ has summarised the position as follows—

“Cresol is a mixture of three isomers. Of the esters with phosphoric acid the *m*- and *p*-isomers are innocuous, but tri-*o*-cresyl phosphate is a dangerously toxic material. It attacks the central nervous system, causing paralysis of the extremities. As little as 0.15 to 0.3 g produces the characteristic symptoms. Poisoning has mainly occurred by consumption of the substance, but some German cases are reported where paralysis has been caused by vinyl sheet plasticised with tricresyl phosphate containing a high proportion of the *o*-isomer. Tri-*o*-cresyl phosphate in liquid form being absorbed through skin, it is advisable to specify not more than 3 per cent. of *o*-isomer in tricresyl phosphate for use in vinyl plastics. Experience has shown no hazards need be anticipated then.”

Certain authorities have taken steps to restrict the proportion of *o*-tolyl ester in tritolyl phosphate. For example, in the Eastern Zone of Germany a limit of 6 per cent. has been set² and in Sweden a limit of 3 per cent. has been advised by Blomqvist.¹ It is understood that a limit of 3 per cent. is being contemplated in America.

Apparently most of the work on toxicity has been concerned with the dangerous character of the tri-*o*-tolyl ester, so although it may be possible at a later date to obtain more precise information about the relative toxicities of tritolyl phosphates of mixed *o*-, *m*- and *p*-esters, it seems desirable at the present time to limit the proportion of *o*-cresol in the mixed cresols used in the preparation of the tritolyl ester, as this will at least limit the proportion of tri-*o*-tolyl ester that can possibly be present in a commercial product. We do not doubt that if the demand arises, it will be possible, at a later date, possibly by infra-red methods, to determine the relative proportions of mixed tolyl esters in the commercial products.

The purpose of this paper, therefore, is to describe the methods that we have found to be most useful in the determination of (a) *o*-cresol in mixed cresols and (b) the *o*-tolyl radicle in commercial samples of tritolyl phosphate. This work is based on previous work of Wurzschnitt,³ who showed that *o*-cresol, when heated with freshly distilled benzaldehyde in the presence of 75 per cent. sulphuric acid, produced a benzein dyestuff of the formula—



This dyestuff is red in acid solution and blue - violet in alkaline solution. Under corresponding conditions *m*- and *p*-cresol do not give coloured products. In our hands Wurzschnitt's method failed in several respects and we have had to modify his test in at least five important particulars, as follows.

Method of extraction and purification of the mixed cresols from the hydrolysis products of tritolyl phosphate—After the hydrolysis of the tritolyl phosphate we find it necessary to extract with ether, first on the alkaline side in order to remove interfering substances, then on the acid side in order to extract the resulting cresols. The residue of cresols obtained on removal of the ether solvent is not a satisfactory product for benzaldehyde condensation and requires purification by distillation.

Conditions of temperature, time, acid concentration and so on used in the condensation with benzaldehyde—These conditions must be well defined and strictly adhered to in order to obtain a resinous condensation product that is completely soluble in methanol.

Extraction and purification of the condensation product and its subsequent solution—After careful washing, the condensation product contains a small amount of sulphuric acid that in its turn produces a small amount of sodium sulphate when made alkaline in the colorimetric test. It is necessary to pay strict attention to the ratio of methyl alcohol to water used at this stage of the procedure in order that any traces of sodium sulphate produced do not interfere in the colorimetry.

Method of preparation of standards—In Wurzschnitt's paper but little attention was paid to the preparation of standards. In our work, the colour standards have been prepared from known amounts of *o*-cresol mixed with a known amount of *m*- and *p*-cresols, free from *o*-cresol.

Use of the Spekker absorptiometer and Lovibond colour disc in the final colour comparison—Wurzschnitt gives no detailed information about the method used to effect colour comparison of the *o*-cresol - benzaldehyde condensation product. In the method that we normally use the final colour comparison is made with a Spekker absorptiometer, the range covered being from 0 to 12 mg of *o*-cresol per 50 ml of coloured solution. With the co-operation of The Tintometer Ltd., two colour discs have been prepared to cover the range 0 to 12 mg of *o*-cresol per 50 ml of coloured solution in 13 steps, and it is suggested that these discs may be of value in the day-to-day control of the quality of mixed cresols used for the preparation of tritolyl phosphate.

The observations of Mr. G. J. Chamberlin of The Tintometer Ltd. on the colours obtained may be of interest. In his view, with low concentrations of *o*-cresol the colour obtained is predominantly yellow. With increasing amounts of *o*-cresol the colour then changes through a greenish grey to a dirty mauve. This appears to be a dichroic solution with two absorption bands that change in relative importance as the concentration increases.

The method that we have evolved for the determination of the proportion of *o*-tolyl esters in tritolyl phosphate is given below. It should be remembered that it is the *o*-cresol content of the mixed cresols recovered from the tritolyl phosphate that is determined, and it is inferred that this figure is precisely the same as the calculated proportion of the tri-*o*-tolyl ester in the original tritolyl phosphate under test.

METHOD

REAGENTS—

Cellosolve potash, 50 per cent. w/v—Dissolve 12.5 g of potassium hydroxide pellets in 25 ml of ethylene glycol mono-ethyl ether by heating under reflux for 5 minutes in the hydrolysis flask.

Sulphuric acid—Diluted (1 + 1) and 75 per cent. v/v.

Ether.

Sodium sulphate—Anhydrous.

Benzaldehyde—Redistil AnalaR grade.

Ammonium hydroxide, 0.5 per cent. w/v—Dilute 20.5 ml of ammonium hydroxide, sp.gr. 0.880, with water to 1 litre.

Methyl alcohol.

Sodium hydroxide, 10 per cent. w/v.

PROCEDURE FOR THE HYDROLYSIS OF THE TRITOLYL PHOSPHATE AND EXTRACTION OF THE RESULTING CRESOLS—

Heat 4 g of the sample with 25 ml of Cellosolve potash under reflux for $2\frac{1}{2}$ hours. Cool the solution and dilute with 150 ml of distilled water, and then extract successively with two 25-ml portions of ether; discard the extracts. Acidify the aqueous layer by the dropwise addition of diluted sulphuric acid (1 + 1) with cooling and extract the acid solution successively with two 25-ml portions of ether; wash the combined ether extracts twice with 50-ml portions of distilled water and dry over anhydrous sodium sulphate before evaporation of the bulk of the ether on a water-bath. Transfer the residual cresols to a small (10-ml) distillation flask and distil. After the preliminary removal of the remaining ether, collect the fraction distilling to the dry point.

PROCEDURE FOR CONDENSATION WITH BENZALDEHYDE—

Transfer 14 drops (about 0.3 g) of the mixed cresols to the bottom of a 6-inch by $\frac{1}{2}$ -inch hard-glass test tube. Weigh the test tube before and after the addition of the cresols. Add 14 drops of redistilled benzaldehyde and mix thoroughly with the weighed amount of mixed cresols. Immerse the tube and contents to a depth of 2 inches in an oil-bath maintained at $130^{\circ} \pm 1^{\circ} \text{C}$. After half a minute, add 5 ml of 75 per cent. v/v sulphuric acid dropwise over a period of 1 minute, with constant stirring by means of a glass rod. Allow the test tube and contents to remain in the oil-bath for a further minute; *i.e.*, the total time of immersion should be $2\frac{1}{2}$ minutes.

After cooling for 20 minutes dilute the mixture with 10 ml of distilled water and filter through a compressed cotton-wool pad in a small porcelain Gooch crucible, 3.5 cm by 2 cm, suction being applied by means of a water pump. With a glass rod, thoroughly break up the insoluble residue on the pad and wash it carefully with at least 100 ml of cold water. This operation is very important, as it is desirable to remove occluded sulphuric acid at this stage. Wash the resin with 40 ml of water at 50° to 60°C , then with 2 ml of 0.5 per cent. w/v ammonium hydroxide and finally with cold water.

Transfer the crucible and contents to a flat-bottomed flask, of 100-ml capacity and with a 3-cm neck, and heat under reflux for 10 minutes with 15 ml of methanol to dissolve the resin. Filter the solution of the resin through a 3-cm Whatman No. 1 filter-paper supported by a filter disc contained in a funnel over a side-arm boiling-tube graduated at 30 ml. Wash the flask and crucible with methanol until the volume of the filtrate is 30 ml.

COLORIMETRY—

Transfer 20 ml of this methanol solution, by means of a pipette, to a 50-ml standard flask. Add 0.5 ml of 10 per cent. w/v sodium hydroxide solution and 12 ml of distilled water. Mix and dilute the solution to the mark with methanol. Filter this solution through a Whatman No. 42 filter-paper into a 1-cm cell and measure the colour in a Spekker absorptiometer 15 minutes after making alkaline and diluting to the mark. Use spectrum yellow filters, No. 606, and Calorex heat absorbers. For the blank use a 75 per cent. v/v solution of methanol in water.

From mixtures made by adding known weights of *o*-cresol to a 50 per cent. w/w mixture of *m*- and *p*-cresol, prepare by the above procedure a calibration curve to cover the range 0 to 12 mg of *o*-cresol per 50 ml of final coloured solution, *i.e.*, from 0 to 6 per cent. of *o*-cresol on a 0.3 g sample. From this curve or from the appropriate Lovibond disc deduce the *o*-cresol content of the unknown cresol mixture. Should the cresols contain more than 6 per cent. of *o*-cresol, a proportionately smaller sample should be taken and diluted to approximately 0.3 g with the 50 per cent. w/w mixture of *m*- and *p*-cresol before the condensation with benzaldehyde. The percentage of *o*-cresol found is assumed to be equivalent to the tri-*o*-tolyl phosphate content of the tritolyl phosphate originally submitted to test.

A typical calibration curve is a straight line passing through the following points—

Indicator drum reading	0.002	0.058	0.115	0.170	0.226	0.284	0.340
<i>o</i> -Cresol corresponding to 50 ml of									
coloured solution, mg	0	2	4	6	8	10	12

NOTES

In the course of the work certain other conclusions have been reached and they may be of interest.

Efficiency of hydrolysis—It has been shown that the hydrolysis of the tritoly! phosphate with Cellosolve potash is very efficient. In given experiments less than 0.2 per cent. of the tritoly! phosphate remained unhydrolysed at the conclusion of the operation.

Interference of phenol and xylenols—The interference of phenol and 2:3-, 2:4-, 2:5-, 2:6-, 3:4- and 3:5-xylenols in the test has been investigated. We are indebted to Mr. P. J. C. Haywood for the supply of authentic samples of these xylenols. There is no interference from 2:3-, 2:4-, 2:5-, 3:4- and 3:5-xylenols, but 2:6-xylene! and phenol do interfere in the test. The magnitude of the interference is demonstrated by the fact that 3 per cent. of phenol would be reported as 1.8 per cent. of *o*-cresol and 3 per cent. of 2:6-xylene! would be reported as 3.6 per cent. of *o*-cresol if examined as unknown samples. In the examination of commercial material it is unlikely that this interference would prove to be serious, as we understand that the maximum 2:6-xylene! content of commercial cresylic acid is of the order of 0.3 per cent. and the maximum phenol content is of the order of 1 per cent.

Flasks—The hydrolysis with Cellosolve potash proceeds smoothly in soda-glass flasks and the life of these flasks is satisfactory. In contrast, Pyrex flasks do not withstand the conditions of the test and should not be used.

Stability of colour—The condensation product is not stable if allowed to stand for a long time in methanol solution, so the colorimetry should be completed within 3 hours of dissolving the resin in methanol. Throughout the test the same time intervals should be used for the samples as are used in the preparation of the standard colour.

REFERENCES

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WELWYN GARDEN CITY, HERTS.

August, 1951