On the Use of the Dimethyl Terephthalate/Dimethyl Isophthalate Recrystallization Residue as a Raw Material in the Production of Solid Polyurethane Foams with Reduced Flammability

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Synopsis

The residue from the recrystallization of the dimethyl terephthalate/dimethyl isophthalate fraction consists mainly of the dimethyl esters of the phthalic acids (ca. 82–85%) and about 15% aldehydes. It is shown that the isophthalic fraction affords the hydroxyl group containing phosphonates on treatment with diethyl phosphite in the presence of alkaline or peroxide catalysts. The residue treated in this manner can be used for preparing oligoester alcohols and solid polyurethane foams from them with reduced flammability.

INTRODUCTION

In the recrystallization of the dimethyl terephthalate/dimethyl isophthalate fraction obtained in the production of dimethyl terephthalate via air oxidation of *p*-xylene and subsequent esterification with methanol is formed a waste product. The fraction consists mainly of dimethyl phthalates, about 85%, the rest being aldehydes. It has been found[1] that this waste fraction can be used as a starting material in the synthesis oligoester alcohols of interest in the synthesis of solid polyurethane foams.

The aim of the present work was to examine the possibility of converting the aldehydes present in the dimethyl terephthalate/dimethyl isophthalate fraction via the Abramov reaction into phosphorus-containing monomers. These latter compounds are known to improve the resistance to combustion of a rigid polyurethane foam based on an oligoester alcohol obtained from a treated in this manner isophthalic fraction.

EXPERIMENTAL

Starting Materials. Residue from the recrystallization of the dimethyl terephthalate/dimethyl isophthalate fraction (isophthalic fraction) with the following composition (see Table I); diethyl phosphite (Fluka commercial product, $n_D^{20°C} = 1.4078$).

Journal of Applied Polymer Science, Vol. 29, 577–582 (1984)
 CCC 0021-8995/84/020577-06$04.00

TABLE I
Composition of the Residue from the Recrystallization of the Dimethyl Terephthalate/Dimethyl Isophthalate Fraction (Isophthalic Fraction)

Name of components of the isophthalic fraction	Composition (%)	
	Before distillation	After distillation
First unknown fraction	0.06	0.0
Methyl benzoate	0.99	0.71
Methyl *p*-toluylate	4.00	4.00
Second unknown fraction	0.03	0.0
Terephthalic aldehyde	4.56	4.56
Second aldehyde	7.05	7.05
Dimethyl terephthalate	15.31	16.55
Dimethyl isophthalate	51.97	52.20
Dimethyl orthophthalate	15.20	14.10
High boiling compounds	0.83	0.83

Addition of Diethyl Phosphite to the Aldehydes from the Isophthalic Fraction

In a four-necked flask provided with a stirrer, thermometer, reflux condensor, and a nitrogen inlet are placed isophthalic fraction (100 g, containing 11.56% of aldehydes) and diethyl phosphite (30 g, 0.22 mol). A saturated sodium ethoxide solution (20–25 mL) is added dropwise to the warmed to 60°C reaction mixture (at this temperature the mixture turns homogeneous). The reaction mixture is then heated to 140°C and kept at this temperature for 6 h. After that, the temperature is decreased to 80°C, and the unreacted diethyl phosphite distilled of under reduced pressure (3 mm Hg).

The experiment was also carried out in the presence of benzoyl peroxide as catalyst (3 g) and at a temperature of 180°C. The composition of the isophthalic fraction after treatment with diethyl phosphite is given in Table II.

Synthesis of Oligoester Alcohol Based on Isophthalic Fraction Treated with Diethyl Phosphite, Diethyleneglycol, and Trimethylolpropane in a Mole Ratio of 1:0.5:2 (Ratio of OH/$COOCH_3$ = 3.5:1)

In a four-necked flask provided with a stirrer, thermometer, reflux condensor, and nitrogen inlet are placed isophthalic fraction with a methoxycarbonyl content of 32.98% (194 g), diethyleneglycol (53 g, 0.5 mol), and trimethylolpropane (268 g, 2 mol) and tetrabutyl titanate (0.65 g) as catalyst. The reaction is conducted at first at 190°C and, after the evolution of methanol decreases the temperature, is brought to 235°C and kept there for 2 h.

The product obtained was characterized by hydroxyl value, acid value, methoxycarbonyl content, viscosity, and presence of diethyleneglycol, moisture, and phosphorus (see Table III).

Synthesis of a Rigid Polyurethane Foam

Preparation of Component A. Oligoester alcohol based on the isophthalic fraction treated with diethyl phosphite (80 parts by weight), polyethyleneglycol (mol mass 200) (15 parts by weight), glycerol (5 parts by weight), dimethyl cyclohexylamine (1 part by weight), dibutyltin dilaurate (0.01 part by weight), water

TABLE II
Composition of the Isophthalic Fraction Treated with Diethyl Phosphite

Name	Initial	Composition (%) After treatment with diethyl phosphite in the presence of catalyst: Saturated sodium ethoxide solution	Benzoyl peroxide
Methyl benzoate	0.71	0.80	0.71
Methyl *p*-toluylate	4.00	4.00	4.00
Terephthalic aldehyde	4.56	0.20	1.45
Second aldehyde	7.05	0.41	1.01
Dimethyl terephthalate	16.55	16.58	19.71
Dimethyl isophthalate	52.20	62.53	60.58
Dimethyl orthophthalate	14.10	15.35	13.84
Highly boiling admixtures	0.83	0.13	0.80

(0.5 part by weight), and freon-11 (30 parts by weight). All ingredients are well mixed.

Component B: Polymeric Diphenylmethane Diisocyanate. The rigid polyurethanes were prepared in a 250-mL beaker by mixing 50 parts by weight of component A with 50 parts by weight of component B. The two components were stirred with a propeller stirrer and the mixture poured onto a polyethylene foil.

Characterizations

(a) The isophthalic fraction treated with diethyl phosphite: aldehydes content by gas chromatography; acid value by titration with potassium hydroxide.

(b) The oligoester alcohol: hydroxyl value by the acetylation procedure; moisture by the Fischer procedure; methoxycarbonyl group content—by gas chromatography; viscosity by using a rotatory viscosimeter type.

The characteristics of the rigid polyurethane were determined by standard procedures.

The oxygen index was evaluated using samples with dimensions of 100/10/10 mm on an FTA instrument.

The thermal studies were conducted on an MOM Derivatograph at a rate of heating of 10°C/min in air.

RESULTS AND DISCUSSION

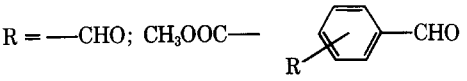
The isophthalic fraction formed in the production of dimethyl terephthalate is of interest as a starting material in the production of various products. Its

TABLE III
Characteristics of an Oligoester Alcohol Synthesized from the Isophthalic Fraction Treated with Diethyl Phosphite

Acid value (mg KOH/g)	380
Acid value (mg KOH/g)	8.16
Moisture content (%)	0.08
Methoxycarbonyl group content (%)	4.1
Diethyleneglycol content (%)	6.0
Phosphorus content (%)	2.54
Viscosity (cps) at 40°C	19,000

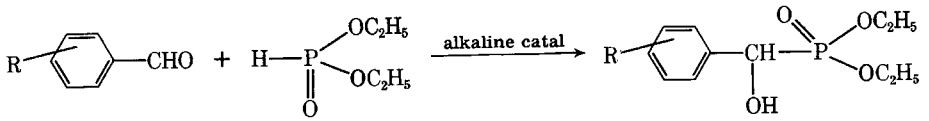
transesterification with diols and triols[1] leads to a hydroxyl-group containing product employed in the synthesis of rigid polyurethane foams. This use of the isophthalic fraction is quite promising since it is known that the rigid polyurethanes prepared on the basis of polyester alcohols are of low toxicity, improved resistance to combustion, and high resilience.[2] A significant drawback of the polyurethane foams is their poor resistance to combustion, which is corrected by introducing phosphorus and phosphorus and chlorine-containing compounds.

As was mentioned above, the isophthalic fraction consists of the addition to the dimethyl phthalates (about 82–85%) also of about 15% aldehydes in which



The presence of aldehydes in the isophthalic fraction provides a possibility of introducing phosphorus in its content via the Abramov reaction.[3]

The following process takes place on treating a preliminarily distilled isophthalic fraction with diethyl phosphite in the presence of basic or peroxide catalysts:



Arising as a result of these interaction monomers are phosphonates which thus act as highly effective fire retardants.

Converting the aldehydes in the isophthalic fraction into phosphonates improves, on the one hand, the resistance of the polyurethanes to combustion while, on the other hand, decreasing the free aldehydes content, since it is known that the aldehydes react with isocyanates at temperatures of about 190°C, which are considerably higher than the temperature at which polyurethanes are synthesized.[4]

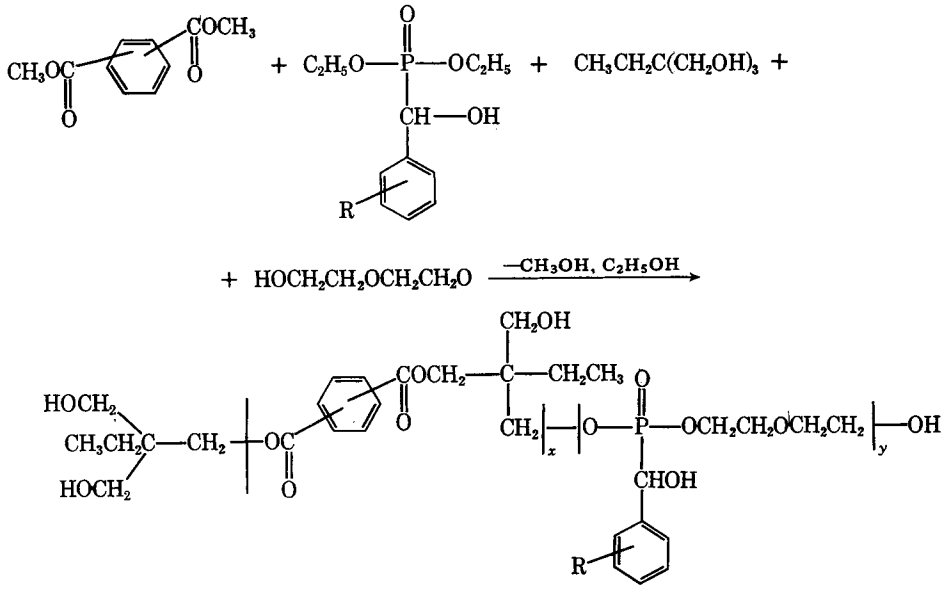
The gas-chromatographic analysis of the isophthalic fraction treated with diethyl phosphite indicates that the aldehyde content is decreased in the presence of a saturated sodium ethoxide solution as a catalyst in amounts between 0.61% and 11.61% or benzoyl peroxide between 2.45% and 11.61% (see Table II).

The decrease in the aldehyde content is due to the Abramov reaction proceeding after treatment of the isophthalic fraction with diethyl phosphite. An indication of this is the phosphorus content (4.49%) of the isophthalic fraction after the treatment.

The results obtained show that the sodium ethoxide is a better catalyst than benzoyl peroxide. The acid value of the isophthalic fraction increases from 10 mg KOH/g with sodium ethoxide as catalyst to 13.3 mg KOH/g and with benzoyl peroxide as catalyst to 49.3 mg KOH/g. This increase in the acid value when using benzoyl peroxide as catalyst is probably due to the conditions under which the synthesis is carried out. It is known[5] that the dialkyl phosphites undergo changes at higher temperatures giving rise to products containing acidic functions.

The gas-chromatographic analysis indicates that the treatment with diethyl

phosphite of the isophthalic fraction affords the addition product I in about 11% yield. The isophthalic fraction obtained in this way was further employed in the preparation of an oligoester alcohol via transesterification with diols and triols:



It is well known[5] that the phosphonic acid esters (and the addition product I is such a compound) can be transesterified with the hydroxyl group containing compounds at temperatures of about 160–170°C, that is, at the conditions of synthesizing the oligoester alcohol they will participate in the transesterification process.

An oligoester alcohol with the following characteristics was synthesized by transesterifying with diethyl phosphite the isophthalic fraction (see Table III).

From the oligoester alcohol obtained in this manner was prepared a rigid polyurethane foam (Table IV). Its oxygen index (22.6% O_2) indicates that it has an improved resistance to combustion, the self-extinguishing properties being due to the presence of phosphorus since rigid polyurethane foams based on polyester alcohols have oxygen indexes of about 19% O_2. The presence of phosphorus does not impair the resilience at 10% deformation. The value of this characteristics is higher than the required by the standard (1.05).

The thermooxidative stability was also examined. It was found (see Fig. 1) that the polyurethane foam begins to decompose at 140°C. The TG curve clearly

TABLE IV
Characteristics of the Polyurethane Foam Based on an Oligoester Alcohol from the Isophthalic Fraction Treated with Diethyl Phosphite

Density (kg/cm^3)	28.2
Resistance to pressure at 10% deformation (kg/cm^3)	1.34
Open/closed pores (%)	92
Phosphorus content (%)	0.56
Oxygen index (%), O_2	22.6

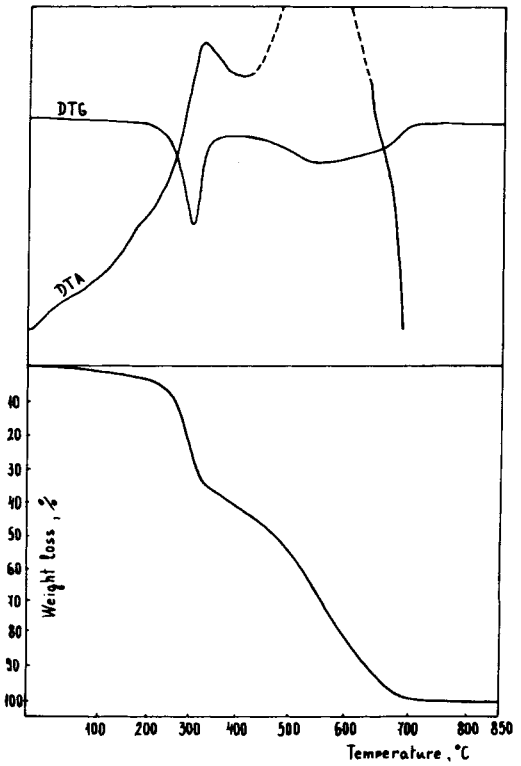


Fig. 1. TG, DTG, and DTA plots for polyurethane.

depicts four decomposition stages, i.e., first till 250°C characterized by a loss of its weight of about 6%; the second between 250°C and 330°C in which the weight loss is 36% (this stage coincides with the maximal rate of decomposition which is observed at 310°C); the third stage is from 330°C till 500°C and is accompanied by a weight loss of 53%; the fourth stage is between 500°C and 700°C. Till 700°C the polyurethane loses 100% of its weight.

The results obtained in the present study show that the introduction of phosphorus in the oligoester alcohol prepared on the basis of the isophthalic fraction from the dimethyl terephthalate production via the Abramov reaction is quite promising since the phosphorus-containing monomer obtained improves the flame-retardant properties of the polyurethane foam based on it.

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Received January 28, 1983
Accepted July 22, 1983