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Synthesis of Esters of Dioxane Alcohols and Their Performance as Plasticizers for Polyvinyl Chloride Compounds

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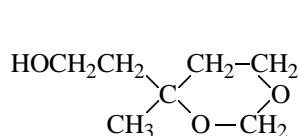
Abstract—A procedure was developed for preparing a plasticizer for polyvinyl chloride compounds from the fraction of dioxane alcohols. The main physicochemical properties of the new plasticizer were determined. Items prepared from formulations containing the new plasticizer were fabricated and tested in laboratory.

Since the discovery of the dioxane method for preparing isoprene, the utilization or reprocessing of dioxane alcohols has been topical problem.

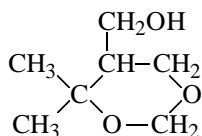
The world's annual production of isoprene reaches now 1000–1100 thousand tons, of which 250 thousand tons (23–25% of the total amount) is produced by the dioxane method. In Russia, the annual production of isoprene is 700–800 thousand tons, of which 190 thousand tons (24–27% of the total amount) is produced by the dioxane method. In this method, the amount of dioxane alcohols (by-products) reaches 100–110 kg per ton of isoprene. Thus, formation of large amounts of dioxane alcohols is inevitable [1].

The fraction of dioxane alcohols from the production of isoprene rubber is a colorless or light yellow mobile liquid containing 50–70 wt % dioxane alcohols; the boiling onset temperature is no less than 225°C, and the flash point, no less than 120°C. The fraction belongs to hazard class 3, recommended value of MPC (with respect to dioxane alcohol) 10 mg m⁻³, LD₅₀ for mice 2700 mg kg⁻¹ [2].

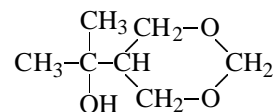
The fraction of dioxane alcohols contains three isomeric alcohols:



4-Methyl-4-hydroxyethyl-1,3-dioxane (I)



4,4-Dimethyl-5-hydroxymethyl-1,3-dioxane (II)



5-(1-Methyl-1-hydroxyethyl)-1,3-dioxane (III)

The major component (60–70% of the sum of the isomers) is 4-methyl-4-(2-hydroxyethyl)-1,3-dioxane I.

A number of possible applications of dioxane alcohols have been outlined in the literature: as an efficient solvent for nitrocellulose, nitrocellulose lacquers, rosin, lac, for bakelite, epoxy, and polyvinyl chloride resins, and for insulating lacquer; as a component of epoxy hardener [3–8]. One of promising ways of processing of the fraction of dioxane alcohols is preparation of plasticizers for polyvinyl chloride resins and rubbers [9–13].

However, proper utilization of this large-tonnage waste remains a matter of current interest.

We believe that the presence of hydroxy and acetal groups in molecules of dioxane alcohols, their low toxicity, absence of odor and color, and high boiling and flash points make these compounds interesting both as objects for theoretical studies (reactivity) and as potential raw materials for chemical industry.

Our goal was to examine the possibility of preparing esters from dioxane alcohols and carboxylic acids, as potential plasticizers.

EXPERIMENTAL

Esters of dioxane alcohols were prepared by two procedures.

(1) Carboxylic acids (acetic, adipic, phthalic, butyric, oxalic) were esterified with dioxane alcohols in the presence of acid catalysts (sulfuric, phosphoric, benzenesulfonic acids; KU-23 cation exchanger). The reactions were performed at 140–165°C for 4–6 h in an excess of dioxane alcohols (molar ratio 4:1). The acid conversion did not exceed 30%; the reaction mixture was dark.

(2) It was suggested to prepare esters of dioxane alcohols by ester interchange catalyzed by both acid and base catalysts, and also by transition metal salts [14].

The latter procedure involved two steps: esterification of adipic acid with butanol to obtain dibutyl adipate and ester interchange of dibutyl adipate with dioxane alcohols.

Esterification of adipic acid was performed with an excess butanol; concentrated sulfuric acid was used as a catalyst. The temperature was maintained within 90–117°C, which enabled distillation of the azeotrope. The concentration of adipic acid in the reaction mixture was monitored titrimetrically [15].

The reaction was stopped at a 98% conversion of adipic acid. Then the mixture was cooled and washed to neutral reaction. Water and excess alcohol were removed from the resulting crude ester by distillation at atmospheric pressure. The ester was distilled at 15 mm Hg; the fraction boiling at 210–213°C was collected. The dibutyl adipate obtained was analyzed for the acid number by the standard procedure [18]. The acid number of dibutyl adipate should not exceed 0.05 (mg KOH) g⁻¹. A higher acid number results in darkening of the reaction mixture in the step of ester interchange of dibutyl adipate with dioxane alcohols.

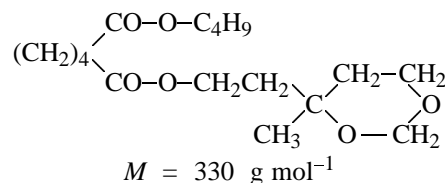
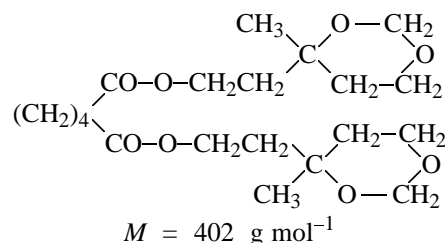
The ester interchange of dibutyl adipate was performed in an excess of dioxane alcohols in the temperature range 215–250°C, so as to ensure continuous distillation of the released butanol at a vapor temperature of 117–120°C. The released butanol can be returned to the step of esterification of adipic acid. As catalyst we used zinc stearate.

The completeness of the ester interchange was judged from the amount of the butanol released. The reaction was stopped at a 85–90% conversion of dibutyl adipate.

From the reaction mixture, we distilled off low-boiling components; the remaining target product

(light yellow mass) was a mixture of esters of adipic acid and dioxane alcohols, with an admixture of dibutyl adipate and zinc stearate. The product yield was 97% of the theoretical value; the content of the mixture of the esters was no less than 98%.

The qualitative analysis of the product was performed by GC/MS on a Finnigan Trace DSQ device in the chemical ionization (isobutane) mode (in the electron impact mode, the molecular ions were not recorded). For the major components, we obtained *m/z* 331 and 403 ([M + H]⁺), which corresponds to the molar weights of the following compounds:



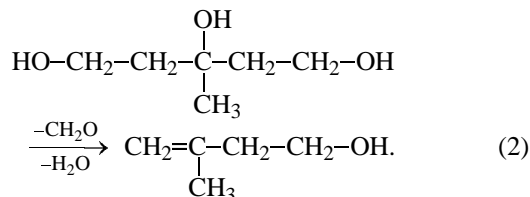
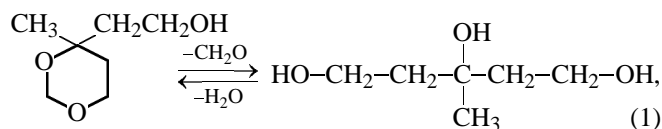
Thus, ester interchange of dibutyl adipate with dioxane alcohols yields a mixture of isomeric mono- and disubstituted esters.

To evaluate the plasticizing power of the product, we prepared samples of the middle PVC layer of calender-rolled linoleum. The samples had the following composition (%): PVC 51, chalk 21, dioctyl phthalate 13, test plasticizer 13, and calcium stearate 2.

As the lower layer we used cotton underwarp (Netkol). A PVC film with a printed pattern is applied onto the upper layer; all the three layers are doubled on a Bersdorf continuous press.

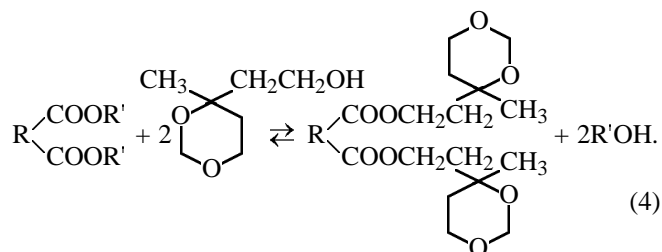
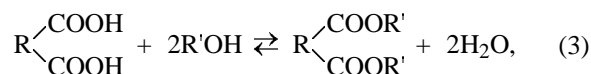
The plastic compound was prepared from a suspension PVC, special stabilizers and pigments, and the test plasticizer (35–40 wt % of the total).

Our experiments showed that esters of dioxane alcohols could not be prepared in reasonable yields and with acceptable quality by esterification with carboxylic acid. Even weak acid catalysts, such as cation exchangers, caused dehydration of dioxane alcohols with ring opening and formation of triols and unsaturated compounds:



Analysis of the reaction mixture shows that dehydration occurs much faster than esterification. Water released in reaction (2) shifts the equilibrium of the target reaction (4), thereby decreasing the yield of the esters. The unsaturated compounds formed in the process undergo condensation, yielding tarry products which impair the quality of the esters.

The two-step procedure we suggested involves the following reactions:



In the first step (3), adipic acid is esterified with a primary aliphatic alcohol. The second step (4) is

ester interchange of the adipic acid ester with dioxane alcohol. To esterify adipic acid, we used aliphatic alcohols that form heteroazeotropes, so as to continuously remove the released water and thus to reach a high conversion of adipic acid (98–99%).

For the product obtained, we determined the main physicochemical parameters [GOST (State Standard) 8728–77] and compared them with those of commercial analogs (Table 1).

Table 1 shows that the plasticizer prepared from dioxane alcohols is similar in physicochemical properties to high-quality commercial plasticizers, such as dioctyl adipate and dioctyl phthalate, and surpasses EDOS plasticizer, widely used today.

To confirm the plasticizing properties of the product we developed, we tested it in linoleum specimens (Table 2). The analysis showed that polyvinyl chloride (PVC-E, PVC-EP) swells in the suggested plasticizer to form fluid easy-to-apply pastes, thickening with time. We prepared specimens of linoleum and PVC RE-0.4 film (PVC-S : PVC-E = 5 : 1) and benzine-resistant plastic compound PB-BK, using the plasticizer developed.

As can be seen, replacement of EDOS plasticizer in the linoleum formulation with the new plasticizer enhances the strength of binding of the face layer and underwarp with the PVC layer. The ready linoleum exhibits higher tensile strength and higher elasticity.

With dioctyl phthalate replaced in the formulation of PB-BK benzine-resistant plastic compound with the new plasticizer, the compounding is quite feasible and the hardness and strength are enhanced relative to the commercial specimens; the benzene resistance remains high (see Table 3).

Table 1. Comparison of the physicochemical properties of the polyester plasticizer prepared in this study with those of commercially used plasticizers

Parameter	Dioctyl adipate	Dioctyl phthalate	EDOS, grade I	Plasticizer prepared
Flash point in open crucible, °C, no less than	190	205	150	216
Weight fraction of volatiles, wt %	0.07	0.1	0.25	0.2
Acid number, (mg KOH) g ⁻¹	0.01	0.05	0.1	0.1–0.3
Density at 20°C, g cm ⁻³	0.92	0.98	1.08	1.1
Saponification number, (mg KOH) g ⁻¹	298–307	284–290	–	350–364
Solidification point, °C	–	–55	–35	–50
Compatibility with PVC	Full	Full	Partial	Full

Table 2. Comparison of linoleum specimens prepared using the plasticizer developed in this study and EDOS

Parameter	Pre-scribed value	Specimen no. 1 (plasticizer developed)	Specimen no. 2 (EDOS)	Testing procedure
Strength of binding between face layer and PVC layer, kgf cm ⁻¹ , no less than	0.6	Longitudinal, 3.09 Transverse, 2.99	Longitudinal, 0.8 Transverse, 0.9	TU 5771-028-00282323-01 (PVC linoleum)
Strength of binding between the PVC layer and underwarp, kgf cm ⁻¹ , no less than	0.2	Longitudinal, 2.4 Transverse, 1.92	Longitudinal, 1.0 Transverse, 1.1	TU 5771-028-00282323-01 (PVC linoleum)
Absolute residual deformation, mm, no more than	1.0	0.55 0.35	0.47	TU 5771-028-00282323-01 (PVC linoleum)
Layer density, g cm ⁻³	–	1.25	1.39	GOST (State Standard) 11529
Breaking tensile stress, N cm ⁻¹ , no less than	215	416	–	TU 2245-016-00282323-98 (film material)
longitudinal	196	458	–	
transverse				
Changes in linear dimensions, %, no more than	1.0	Longitudinal, 0.4 Transverse, 0.3	Longitudinal, 0.11 Transverse, 0.08	TU 5771-028-00282323-01 (PVC linoleum)
Layer thickness, mm, no less than	1.3	1.69	1.96	TU 5771-028-00282323-01 (PVC linoleum)

* (TU) Technical specifications; the same for Table 3.

Table 3. Comparison of the properties of PB-BK plastic compound prepared with the plasticizer developed and with dioctyl phthalate

Parameter	Prescribed value	With plasticizer developed	With dioctyl phthalate	Testing procedure
Shore hardness, units	80 ± 0.5	80	79	TU 2246-022-00282323-01 (plastic compound for PVC tubes)
Benzine resistance, %, no more than	1.6	0.1	–	TU 2246-022-00282323-01 (plastic compound for PVC tubes)
Tensile strength, MPa, no less than	18.6	19.3	18.9	TU 2246-022-00282323-01 (plastic compound for PVC tubes)

CONCLUSIONS

(1) Previously unknown esters of adipic acid and dioxane alcohols were prepared.

(2) A catalyst for ester interchange of dibutyl adipate with the dioxane alcohol fraction was suggested, and the main process parameters were determined.

(3) The physicochemical properties of the mixture of dioxane alcohol adipates are comparable with those of commercial PVC plasticizers. The new plasticizer can be used for fabricating items with enhanced strength, elasticity, and benzine resistance.

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