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Development of Oil-Benzen-Resistant PVC-Plastics

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Abstract: With the increase in the production of Polyvinylchloride (PVC) products increases the need to improve their performance properties and therefore as a consequence, there is a need for selecting economically beneficial supplements. The solution to this problem is to create effective plasticizers for a great number of PVC materials on the basis of available raw materials. The most used additives such as plasticizers for PVC are phthalates on the basis of which are PVC compositions with enhanced physical-mechanical and operational characteristics. Therefore, the synthesis and study of new effective plasticizers is very relevant and useful for industry. In order to implement this direction, we have obtained asymmetric phthalates oxyalkylated alcohols by two-stage esterification of phthalic anhydride in a single reaction volume. The obtained esters were tested as plasticizers in PVC compounding of the top layer of linoleum. As shown by the results of the tests, all specimens provided the proportionality PVC films relevant technical requirements. Time of thermal stability, melt flow index in all cases, the use of prototypes plasticizers were significantly higher indicating that simplification of the above processing of PVC compositions. It should also be noted that PVC films have superior quantities of oil and gasoline resistant.

Key words: Gasoline, oil resistant, steel phthalates, oxyalkylated alcohols, plasticizers, PVC-formulation

INTRODUCTION

To date, the basis of all polymer products is only a small number of known polymers widely used in medicine, engineering, agriculture as well as in the construction sector and at home. One of such polymers is Polyvinylchloride (PVC) which ranks third in the world in production and consumption after polyethylene and polypropylene. Plastic compounds based on polyvinylchloride are used in various areas for the manufacture of a wide range of materials and products. This is due to the availability of raw materials, rather low cost and extensive opportunities for modifying their properties (Ulyanov *et al*., 1992; Wilke *et al*., 2007; Chalaya, 2006; Mazitova *et al*., 2013).

Adding additives of various functional purposes-plasticizers, stabilizers, fillers, fire retardants, etc, achieves the meaningful change in the characteristics of PVC. The choice of the type and dosage of the initial components is determined by the conditions of processing the polymer composition and the necessary complex of operational properties of the products obtained (Mazitova *et al*., 2013; Maslova, 1981; Barshteyn *et al*., 1982; Tinius, 1964; Karimov *et al*., 1997a, b).

Plasticizers are introduced into the composition of polymers to increase their technological and operational characteristics. A characteristic feature of this group of additives is the imparting to the materials of increased strength at break and a large relative elongation and with a given elasticity that persists in a wide range of temperatures (Mazitova *et al*., 1984, 2013; Barshteyn *et al*., 1982; Tinius, 1964; Maskova, 2012).

In the industry, the most popular plasticizers of PVC are esters. The volume of their production accounts for 85% of the total output of all plasticizers. Esters of phthalic (phthalates), phosphoric (phosphates), sebacic (sebacates) and adipic acids (adipates) are of the greatest practical interest. Phthalates are the largest group of chemical plasticizers used in PVC, most of which are general purpose (Mazitova *et al*., 1984, 2013; Barshteyn *et al*., 1982; Tinius, 1964; Maskova, 2012).

Phthalates is well combined with polymers give them a high physical-mechanical properties. As plasticizers phthalates exhibit excellent compatibility, the required homogenization of the composition and provide a set of performance properties for multiple use, allow minimum modification at the expense of other types of plasticizers. They have good electrical insulating properties, frost, heat and lightfastness. Therefore, the compounds on their basis are widely applied in the construction sector, engineering and also in agriculture and in the home. Besides, these softeners are mainly obtained

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from the available cheap raw materials (Mazitova *et al*., 2014, 2015a, b; Maskova *et al*., 2015; Aminova *et al*., 2012a, b).

Currently di (2-ethylhexyl) phthalate (Dioctyl Phthalate, (DOP)) remains an international standard of PVC plasticizer. Specifications to other plasticizers are coordinated with specification for DOP. Leading position of dioctyl phthalate to this day is determined, above all by the development of production of flexible PVC the largest consumer of DOP. Although, recently the structure of PVC's consumption has changed to the direction of hard manufactures, however, plasticized materials on the base of PVC remain actual in the different fields. DOP plasticizer has good properties: it is resistant to extraction by water and oils has moderate volatility and good performance at low temperatures (Mazitova *et al*., 2015c, d; Faizullina *et al*., 2017; Builova *et al*., 2013; Mazitova *et al*., 1984; Abdrakhmanova *et al*., 2008).

As you know, the fields of application of plasticized PVC in general and market of plasticizers in particular are under strict control of directives of environment and human health. Therefore, effective and most common phthalate plasticizer restricted to use in medical devices, children's toys, food packaging in connection with the research which questioned its safety (Regulation (EU) No. 1907/2006). Problems with the use of the most outstanding representative of the phthalate groups are fundamentally changing the structure of supply and demand.

In relation with before mentioned proportion of DOP consumption tends to decrease gradually. Although, the replacement of DOP by other plasticizers is not always possible because this lead to increase of product cost in addition such properties of product as flexibility and transparency are not always achieved, however, increasing requirements make manufacturers of plasticizers to devote funds to the search and development of other safe plasticizers for PVC compounds.

One of the dynamically developing segments of the polymer industry is the production of oil-and-petrol resistant PVC-plastics which are used for manufacturing a wide range of products-footwear, linoleum, hoses, cable sheaths, artificial leathers, etc. Butylbenzylphthalate (BBzF) is purchased by import as far as in Russia there is no production of butylbenzylphthalate. On the one hand, that is connected with a shortage of raw materials (benzylchloride), on the other hand with the lack of modern technologies for the production of asymmetric phthalic acid esters. Therefore, the development of oil-benzene-resistant PVC plastic compounds with the use of new efficient domestic plasticizers has an important scientific and practical significance.

In the given researcher are sfown results of researches on development of PVC-formulations of the top layer of oil-and-petrol resistant linoleum with the use of new plasticizers-butoxyethylphenoxyethylphthalates butoxypropylphenoxypropylphthalates and benzyloxypr opylbenzylphthalates.

MATERIALS AND METHODS

The desired esters were prepared in two steps. Firstly, oxyalkylated alcohols were synthesized. Then, the esterification with phthalic anhydride gave the final products.

The procedure of oxyalkylation of alcohols: A four-necked retort equipped with a stirrer, thermometer, reflux condenser and device for introducing ethylene oxide (propylene) into the liquid is charged with the calculated amount of alcohol and sodium hydroxide catalyst. The reactor is heated in an oil bath to 110°-180°C and purged with nitrogen to remove air. Then gradually (with the stirrer running) ethylene oxide (propylene) is introduced. The feed rate of ethylene oxide (propylene) is controlled so that unreacted oxide is condensed in a reflux condenser and drained back to the reactor without flooding. After feeding ethylene oxide (propylene), the reaction mixture is heated for a further 1-1.5 h and then cooled to room temperature.

Method of esterification of phthalic anhydride: A phthalic anhydride, an oxyalkylated alcohol and a catalyst, tetrabutoxytitanium are placed in a three-necked flask equipped with a Dean-Stark trap cooler, a thermometer and a mechanical stirrer. The reaction is carried out until the calculated amount of water is formed in the trap. At the end of the reaction, tetrabutoxytitanium is hydrolyzed with water and the esterification is filtered to remove the titanium dioxide formed.

RESULTS AND DISCUSSION

Physicochemical parameters of phthalates of asymmetric oxyalkylated alcohols are given in Table 1 and Fig. 1:

$$R1 = H, R_2 = C_4H_9, R_3 = (CH_2CH_2O)nC_6H_5 \quad (1)$$

$$R1 = H, R_2 = C_4H_9, R_3 = (CH_2CH_2O)nC_6H_5 \quad (2)$$

$$R1 = CH_3, R_2 = C_4H_9, R_3 = (CH_2CHOCH_3)nC_6H_5 \quad (3)$$

$$R1 = CH_3, R_2 = CH_2C_6H_5, R_3 = (CH_2C_6H_5) \quad (4)$$

Table 1: Pysicochemical properties of synthesized estersthe general formula

	No the sample			
Name of the indicators	1	2	3	4
Degree of oxyalkylation of alcohol (n)	2.0	1.5	2.2	1.1
Density (d^{20}_4)	1.1081	1.1054	1.1078	1.1075
Refractive index (n^{20}_D)	1.5183	1.5190	1.5175	1.5189
Acid number (mg KOH/g)	0.2	0.2	0.2	0.2
Ether number (mg KOH/g)	257	271	214	271
Molecular weight, found	436	415	524	413
Freezing point (°C)	-40	-39	-40	-38
Mass fraction of volatile substances (100°C, 6 h) (%)	0.10	0.10	0.10	0.11

Degree of oxyethylation of phenol = 1.0; Degree of hydroxypropylation of phenol = 2.1

Table 2: Effect of plasticizers on the characteristics of the top layer of linoleum

Name of the indicator	The developed plasticizers					
Prototypes	1	2	3	4	BBzF	Norms of local standarts 00203312-100-2006
Tensile strength (kgf /cm^2)						
along	285	273	269	272	299	min. 175
across	249	225	237	240	273	min. 175
Relative elongation at break (%)						
along	260	283	267	254	216	min. 100
across	241	261	254	225	201	min. 100
Change in linear dimensions (%)	1.9	1.5	1.5	1.2	2.6	max. 3.0

Table 3: Technology indicators

Thermal stability at 180°C (min)	1 h 48 min	1 h 33 min	1 h 54 min	1 h 43 min	1 h 05 min	Control with dioctyl phthalate 1 h 45 min
Film-forming plastics material, g/10 min T = 17°C P = 16.6 kgf	8.0	7.5	7.2	7.1	6.4	7.1
Water absorption (%)	0.437	0.474	0.485	0.482	0.204	0.195
Extractability by gasoline (%)	1.53	1.44	1.48	1.21	11.72	13.00
Extractability by oils (%)	9.5	9.7	8.1	7.4	4.35	11.0

Temperature of brittleness (°C), endure = -25

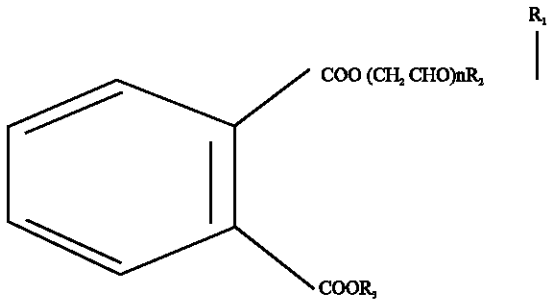

Fig. 1: Parameters of phthalates of asymmetric oxyalkylated alcohols

The esters obtained were tested as plasticizers of polyvinylchloride in the PVC formulation of the upper layer of linoleum (Table 2 and 3). In the formulation of the upper layer of linoleum, the developed plasticizers were introduced in place of butylbenzylphthalate, taking into account the replacement factor.

The obtained PVC films of the upper layer of linoleum were analyzed according to norms of local standards 00203312-100-2006. As the control sample was used BbsF. The results show that the developed plasticizers in comparison with butylbenzylphthalate provide a smaller change in the linear dimensions (shrinkage) of the film (in 7.6-9.7 times) and less extracted with gasoline (1.7-2.2 times). The oil resistance of the test samples is higher than that of the control samples (2.0-2.5 times) but the values obtained in all cases correspond to the established norms. The highest resistance to the action of oils and gasoline has a film obtained with the sample (4).

According to the test results, PVC compositions containing new plasticizers meet the current standards according to the main characteristics and surpass the industrial analogues in terms of oil and gasoline resistance.

Oil-and-petrol polymeric materials are used in various industries. In general, the requirements for polymeric materials is growing and the number of works devoted to the creation of polymeric materials with special requirements increases.

The literature analysis shows that many domestic and Foreign scientists, Voskresensky (1963, 1971, 1977), Tinius (1964), Starkman (1975), Barshteyn *et al.* (1982), Kozlov (1982) and others in his research, paid great attention to developing composite PVC materials. They carried out fundamental research gave the opportunity to form the most important principles in the formulation of polyvinylchloride compositionsand also to evaluate the influence of plasticizers on the properties of polymeric materials.

In the process of creating formulations of PVC compounds that are resistant to aggressive environments, great importance is selection and production of effective plasticizers that meet high modern requirements. To increase the resistance to extraction by gasoline and oils plasticized PVC in the literature, it is proposed to use polyesters and butylbenzylphthalate. However in the writings of these scholars do not address the use of asymmetric phthalate plasticizers (Wilke *et al*., 2007; Mazitova *et al*., 2013; Tinius, 1964; Karimov *et al*., 1997a, b).

Therefore, research in the field of development of effective chemical additives for PVC in our opinion are timely, they aim to study the possibility of creating a combination of new additives for PVC and as a result to receive the finished products. To increase the product range of additives for polyvinyl chloride we synthesized new effective plasticizers phthalates steel on the basis of oxyalkylation of butanols, phenols and phenylcarbinols.

It should also be noted that in the process of creating formulations of PVC compounds that are resistant to aggressive environments, great importance is selection and production of effective plasticizers that meet high modern requirements. This is because due to new requirements of polymer products, problems with the use of many plasticizers alter the structure of supply and demand. So, we also shows the possibility of the directed change of properties of oil-resistant PVC compounds with the use of new plasticizers-butoxyethyl phenoxyethyl phthalates butoxypropylphenoxypropyl phthalates and benzyloxy propyl benzyl phthalates. Researched and shown that the replacement of alkyl groups on the aryl reduces extraction of the mineral oils and petrol.

Thus, we have proposed the solution of urgent scientific and technical tasks, the extension interval of the PVC additives business due to the new domestic steel phthalate plasticizers used in obtaining oil-resistant PVC compounds.

Therefore, we have passed butoxyethyl phenoxy ethyl phthalates, butoxypropylphenoxypropyl phthalates and benzyloxy propyl benzyl phthalates for extensive testing.

CONCLUSION

PVC linoleum is the most common type of flooring. Depending on the type of premises the materials for the flooring meets the highest requirements including resistance to oils and gasoline. Multi-layered linoleum consists of three layers: the lower and the middle which contain significant amounts of filler and the upper transparent. The top layer determines the resistance of the linoleum to abrasion and the action of oils and gasoline.

In practice, to obtain oil-and-petrol linoleum is used, the plasticizer butylbenzylphthalate which is not produced in Russia and is imported. Therefore, we obtained and investigated butoxyethylphenoxyethylph thalates butoxypropyl phenoxy propyl phthalates and benzyloxypropylbenzyl phthalates. In the opinion, the development of new asymmetric phthalate plasticizers and their use in polyvinylchloride compositions, the finishing destination will allow to replace expensive imported analogues and to reduce the cost of oil-and-petrol resistant PVC materials.

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