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NEW PLASTICIZERS FOR PVC-COMPOSITIONS IN CONSTRUCTION

EXTENDED ABSTRACT:

The work is devoted to the analysis and development of effective types of plasticizers for a wide range of finishing (linoleum) and insulating building materials (insulation tape, cable plastic) with improved mechanical and technical characteristics. In connection with the growth of consumption of finishing and insulating materials, the development of new formulations of PVC compositions for construction with the use of new plasticizers is not only an urgent task, but also within the framework of construction it allows solving the problems of effective quality control of a finished PVC composition.

This paper presents the results of the tests of octylphenoxyethylphtalates as a new chemical additives for plasticizing PVC in the formulation of the upper and middle layers of linoleum, adhesive film and cable compound O-40 rec. OM-40 (black). It is noted, that obtained samples of adhesive tape with their main characteristics (tensile strength at break, extension coefficient, shatter point, thermostability) correspond to technical specification (TS) 2245-001-00203312-2003. Obtained samples of plasticate were analyzed according to GOST 5960-72 rev. 1-9 (PVC plasticate for isolation and protective covers of wires and cables), by main characteristics (specific insulation resistance, tensile strength at break, breaking elongation, shatter point) are not inferior to commercial prototypes, and such characteristics as «Weight loss at 160°C» and «Water absorption» are



significantly lower. It is noted that, in case of using octylphenoxyethyl phthalates, obtained samples of films of upper and middle layers of linoleum analyzed according to norms of STI 00203312-100-2006 have a higher melt flow rate. In addition, films obtained through introduction of suggested plasticizers possess a low value of extractability by gasoline and oils.

Keywords: benzene resistance, water absorption, PVC adhesive tape, oil resistance, materials for wire and cable isolation, octylphenoxyethyl phthalates, polyvinylchloride plasticizers, linoleum layer, Shore hardness, thermostability.

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The use of plasticizers in the preparation of polyvinylchloride (PVC) compounds are caused by special characteristics of polymer's chemical structure – low elasticity, wide temperature range of plastic deformation, reduced freezing resistance. For this reason intensification of manufacturing process, expansion of the field of application PVC and providing a wide variety of its properties are connected mostly with successful solution of the problem of effective plasticizers creation [1–5].

Esters of phthalic acid are most consumed plasticizers. Phthalates are well combined with polymers and provide polymers with high physical and mechanical properties: abrasive resistance, low temperature resistance, thermostability, light resistance [1, 2, 6–10].



In this regard, it is not surprising that the task to explore the possibilities to develop the range of plasticizers based on phthalic acid esters are still of great interest among the researchers at the present time.

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 [1, 2, 7, 9, 10]. 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.

Apart from the main plasticizer DOP also the most widely used ester plasticizers include dibutyl phthalate (DBP), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP). However, the wide-scale and most accessible DBP does not provide the long-term exploitation of PVC-compositions. Dibutyl phthalate is high volatile that leads to intensive loss of plasticizer from plasticate, deterioration of physical and mechanical properties and reducing of lifetime of goods made of it. Despite of good low temperature properties at much lower volatility, DINP possesses lower plasticizing capability in comparison with DOP. As distinct from many plasticizers DIDP gives stability at high temperature to finished products, it is resistant to influence of different extractants and has a high heat-resistance, but to achieve the same plasticizing effect and to save other properties of PVC-compositions it is required to introduce to 6% more than DOP. In addition, although diisodecyl phthalate has a more low volatility it is less effective than dioctyl phthalate. It should also be noted that DINP and DIDP are produced in a small scale in our country. The existing deficit of isononyl and isodecyl alcohol (they are not produced by Russian enterprises) impedes the establishment of large-scale production of plasticizers [1, 2, 10, 11].

Recently, 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. Regulations are realized by European Council for Plasticizers and Intermediates. According to the regulations of European Union of Chemicals REACH No 1907/2006 (Registration, Evaluation and Authorization of Chemicals), manufacturers of plasticizers and products with using plasticizers must provide appropriate cer-



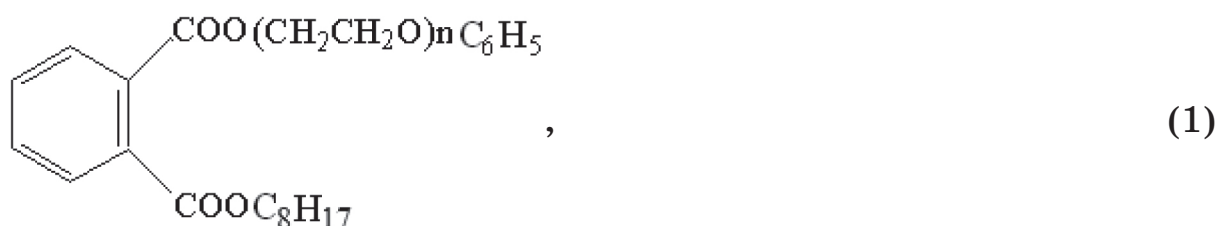
tificates and in case if they are absent, production and sale of these products are prohibited in Europe. The most debating is the question about safety of DOP. According to the expert investigation carried by European scientists, PVC products which are plasticized by DOP were harmful for health. That resulted to ban of production and sale some of products in Europe [11–18].

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, as it leads 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.

In addition, the important part of the problem of creating the PVC-compounds with resistance to aggressive environments is the development of special plasticizers that satisfy modern strict requirements.

For this reason, the development of competitive formulations of PVC compounds meeting the modern ecological, technological and operational requirements with specific properties is relevant and practically important task.

We carry out investigations on development of new plasticizers [19–32]. In this paper the results of the tests of octylphenoxyethyl phthalates (OPOEP) in the formulation of PVC-films of the upper and intermediate layers of linoleum, PVC adhesive tape and cable PVC-compound brand O-40 rec. OM-40 (black) are presented.



where $n = 1, 0-2, 4$.

Suggested synthesized esters as plasticizers of PVC with third class of hazard were prepared by esterification of phthalic anhydride with oxyethylated alcohol by our previously developed methods [19, 22, 23, 25, 31]. The mass content of base substance is 99,0%.

To determine the efficiency of developed plasticizers the changing of Shore A hardness from the concentration of plasticizer were studied (plasticizer:PVC – 1:100). Based on the calculation of quantitative substitution factor (SF), which determine the required quantity of octylphenoxyethyl phtalates in comparison with DOF and which provide a necessary hardness of flexible PVC at room temperature, it was found that experimental prototype I (oxyethylation degree 1,0) is similar to DOP by plasticization efficiency. Selected OPOEP was tested in some of the PVC-compounds of building purpose. Experimental prototype I was introduced instead of commercial analogue – DOP in PVC-formulation. PVC – films of upper and middle layers of linoleum were analyzed according to requirements of CTII 00203312-100-2006. The obtained samples of PVC adhesive tape were analyzed according to TS 2245-001-00203312-2003 (PVC adhesive tape). The obtained samples of cable compounds brand O-40 rec. OM-40

Table 1

The results of tests of experimental films in the industrial composition of upper layer of linoleum

Characteristics		Norms of STI 00203312-100-2006	Control sample	Experimental prototype
Longitudinal strength, kgf/cm ²	along	No less than 175	299	274
	across	No less than 175	273	242
Breaking elongation, %	along	No less than 100	216	256
	across	No less than 100	201	227
Changes in linear dimensions, %		No more than 3,0	2,6	2,2
<i>Technological properties</i>				
Thermostability at 180°C, minute		1 h 45 min	1 h 05 min	1 h 43 min
Melt flow rate, g/10 min T = 170°C, P = 16,6kgf		7,1	7,4	7,1
Shatter point, °C		-25	pass a test	pass a test
Water absorption, %		0,195	0,204	0,480
Extractability by gasoline, %		18,00	11,72	1,52
Extractability by oils, %		11,0	4,35	10,1



Table 2

The results of tests of experimental films in the industrial composition of middle layer of linoleum

Characteristics		Norms of STI 00203312-100-2006	Control sample	Experimental prototype
Longitudinal strength, kgf/cm ²	along	No less than 100	179	176
	across	No less than 100	159	137
Breaking elongation, %	along	No less than 100	251	248
	across	No less than 100	249	236
Changes in linear dimensions, %		No more than 3,0	2,6	2,4
<i>Technological properties</i>				
Thermostability at 180°C, min		37 min	1 h 05 min	1 h 55 min
Melt flow rate, g/10 min T = 170°C, P = 16,6 kgf		9,9	10,0	9,9
Shatter point, °C		-25	pass a test	pass a test
Water absorption, %		0,195	0,204	0,456
Extractability by gasoline, %		18,00	11,72	1,52
Extractability by oils, %		11,0	4,35	10,8

(black) were analyzed according to GOST 5960-72 rev. 1-9 (PVC plasticate for isolation and protective covers of wires and cables). The results of tests are presented in the tables 1–4.

Pictures obtained by scanning electron microscope demonstrate the resistance of linoleum on the base octylphenoxyethyl phthalates to aggressive environments in comparison with commercial plasticizer DOP.

From tests results it is evident that plasticates obtained with introducing octylphenoxyethyl phthalate in the formulation correspond to requirements of GOST and TS by all characteristics, such characteristics as resistance to oil and petroleum are better than in the experimental prototypes.

Thus, as a result of carried research we can say that octylphenoxyethyl phthalates suggested in quality plasticizers can be successfully used in PVC-compositions and have perspective of industrial application.



Table 3

The results of tests of PVC adhesive tape

Characteristics	Norms of TS 2245-001-00203312-2003	Control sample	Experimental prototype
Visual appearance of tape	The tape must not have defects such as inclusions, through holes, breaks	Without defects	Without defects
Tensile strength at break, N/cm	No less than 50	73	72
Extension coefficient, %	No less than 80	277	277
Shatter point, °C	Not above – 30	pass a test	pass a test
<i>Technological properties</i>			
Thermostability at 180°C, min	GOST 14041-91	2 h 37 min	2h 29 min
Melt flow rate, at T = 180°C, H = 16,6 kgf, g/10 min	GOST 11645-73	10,5	13,9

Table 4

The results of tests of PVC adhesive tape brand O-40 пец. OM-40 (black)

Characteristics	Norms of GOST 5960-72 rev. 1-9 (1 quality)	Control sample	Experimental prototype
Specific insulation resistance at 20°C, Ohm·cm	No less than 1·10 ¹⁰	9,0·10 ¹²	6,2·10 ¹²
Tensile strength at break, kgf/cm ²	No less than 110	147	142
Breaking elongation, %	No less than 280	385	278
Shatter point, °C	Not above – 40	выдерживает	выдерживает
Weight loss at 160°C, within 6 h, %	No more than 3,0	2,2	1,7
Hardness, kgf/cm ² , at 20°C	No less than 9–20	12,5	11,9
at 70°C	6–12	7,3	7,4
Water absorption, %	No more than 0,45	0,080	0,052
Softening point, °C	170±10	171	171
Density, g/cm ³	No more than 1,4	1,38	1,38
<i>Technological properties</i>			
Thermostability at 180°C, h	GOST 14041-91	3 h 15 min	3 h 13 min
Melt flow rate, g/10 min at 190°C, P = 10 kgf/cm ²	GOST 11645-73	103,3	102,6



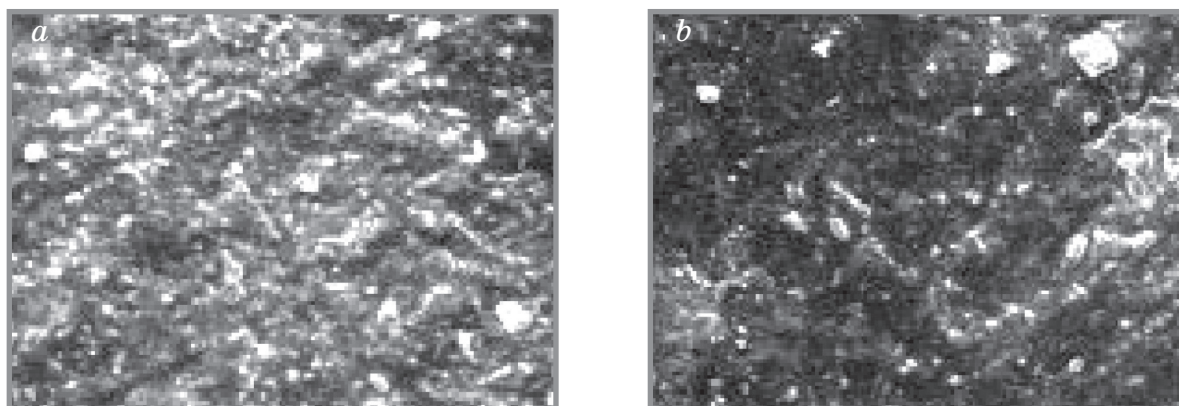


Fig. Optical micrographs of samples of the upper layer of linoleum with octylphenoxyethyl phthalate (a) and DOP (b) (resolution 500)

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НОВЫЕ ПЛАСТИФИКАТОРЫ ДЛЯ ПВХ-КОМПОЗИЦИЙ СТРОИТЕЛЬНОГО НАЗНАЧЕНИЯ

АННОТАЦИЯ К СТАТЬЕ (АВТОРСКОЕ РЕЗЮМЕ, РЕФЕРАТ):

Работа посвящена анализу и разработке эффективных видов пластификаторов для широкой номенклатуры отделочных (линолеум) и изоляционных строительных материалов (изоляционная лента, кабельный пластикат) с улучшенными механическими и техническими характеристиками. В связи с ростом объемов потребления отделочных и изоляционных материалов, разработка новых рецептур ПВХ-композиций строительного назначения с применением новых пластификаторов является не только актуальной задачей, но и в рамках строительства позволяет решать задачи эффективного управления качеством готовой поливинилхлоридной композиции.

В работе приведены результаты испытаний октилфеноксидилфталатов в качестве новых химикатов-добавок при пластификации ПВХ в рецептурах верхнего и промежуточного слоев линолеума, ленты липкой, а также кабельного пластиката О-40 рец. ОМ-40 (черный). Отмечено, что полученные образцы ленты липкой по своим основным показателям – прочность при разрыве, относительное удлинение, температура хрупкости, термостабильность – со-



ответствуют ТУ 2245-001-00203312-2003. Полученные образцы пластика, анализированные согласно ГОСТ 5960-72 с изм. 1-9 (Пластикат поливинилхлоридный для изоляции и защитных оболочек проводов и кабелей), по основным показателям – удельное объемное электрическое сопротивление, прочность при разрыве, относительное удлинение при разрыве, температура хрупкости – не уступают промышленным образцам, а такие показатели как «Потери в массе при 160°C» и «Водопоглощение» значительно ниже. Отмечено, что при использовании октилфеноксипропиленфталатов полученные образцы пленок верхнего и промежуточного слоев линолеума, анализированные согласно СТБ 00203312-100-2006, обладают более высокими значениями текучести расплава. К тому же пленки, полученные с введением в рецептуру предложенных нами пластификаторов, обладают низкими значениями экстрагируемости бензином и маслами.

Ключевые слова: бензостойкость, водопоглощение, лента ПВХ липкая, маслостойкость, материалы для изоляции проводов и кабелей, октилфеноксипропиленфталаты, пластификаторы поливинилхлорида, слой линолеума, твердость по Шору, термостабильность.

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