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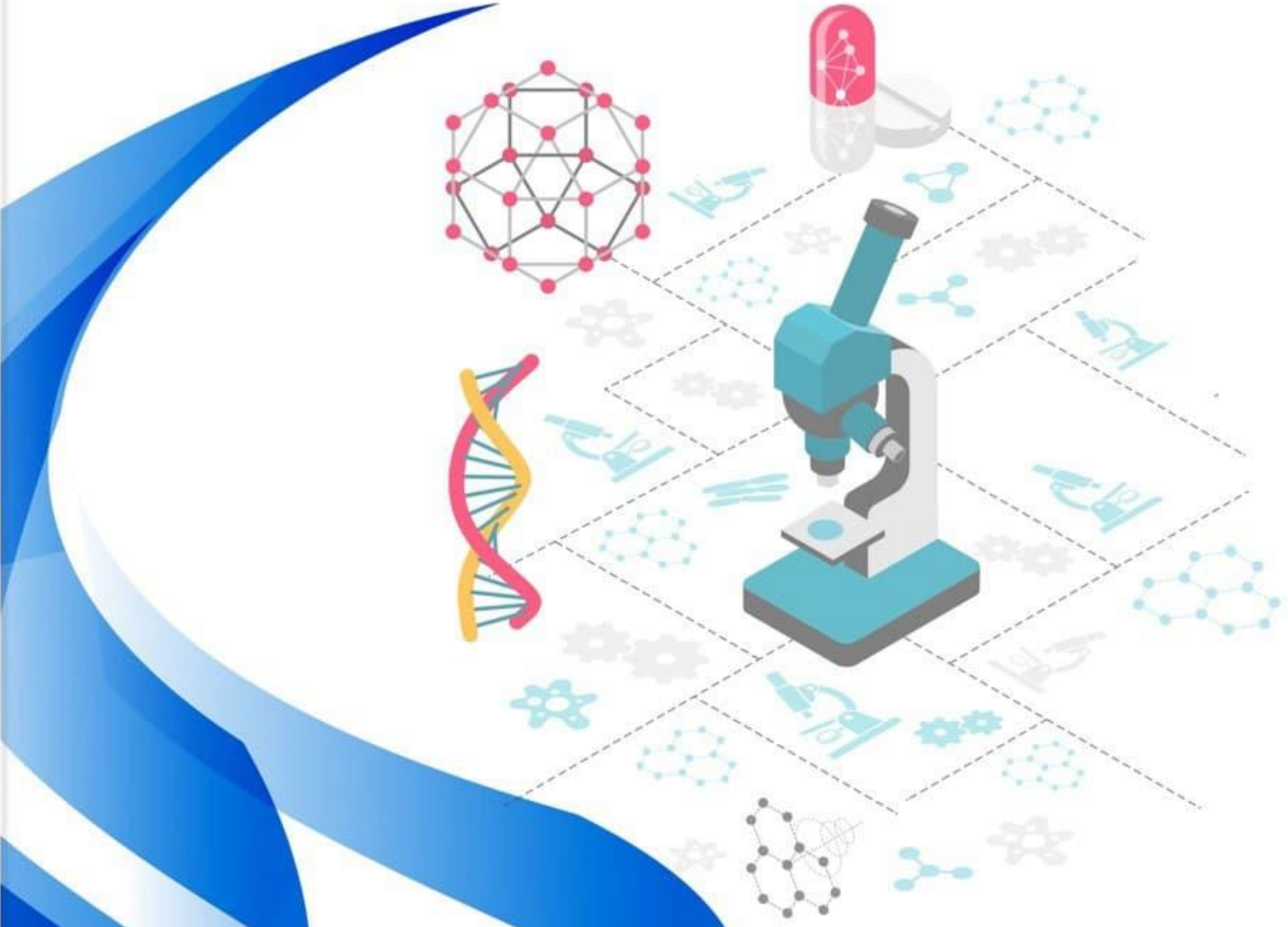

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THERMAL AND THERMO-OXIDATION STABILITY OF POLYVINYL CHLORIDE PLASTICIZED WITH DIOCTYL TEREPHTHALATE

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Abstract. Some aspects of the state of the problem of using diester phthalate plasticizers for polyvinyl chloride plastic compounds are considered. The effect of the plasticizer dioctyl terephthalate on the rate of thermo-oxidative dehydrochlorination of polyvinyl chloride (PVC) has been studied. It has been established that dioctyl terephthalate has a higher thermal and oxidative stability and has a lesser effect on the thermal oxidative degradation of polyvinyl chloride (PVC), in comparison with the plasticizer dioctyl phthalate, which is widely used in the production of PVC. The influence of non-toxic antioxidants - 2,6-di-tert-butyl-4-methyl-phenol (ionol), 4-hydroxy-3.5-di-tert-butylphenylpropionic acid ester (irganox 1010) on the process of accumulation of hydroperoxides and effective dosages of antioxidants were selected to inhibit the process of thermal-oxidative degradation of the polymer. The possibility of complete replacement of the toxic plasticizer dioctyl phthalate with non-toxic dioctyl terephthalate is shown. The use of dioctyl terephthalate stabilized with antioxidants is appropriate to increase the thermal stability and durability of PVC compounds.

Keywords: polyvinyl chloride, dioctyl terephthalate, thermooxidative degradation, dehydrochlorination rate, antioxidant.

Introduction. Polyvinyl chloride (PVC) is one of the world's leading thermoplastics. The main part of polyvinyl chloride is processed into various plasticized materials, in particular, building finishing materials (linoleum, artificial leather, wallpaper, sticky tape), insulating materials, transparent films, decorative oilcloth, etc.

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Plasticizers have a significant impact on the structure and properties of PVC. Using their various types, it is possible to directionally change the characteristics of a polymer material: strength, hardness, frost resistance and brittleness, impact strength, rheological, electrophysical, and other properties of polymers [1–6].

The successful selection of a plasticizer expands the scope of polymers and increases their service life. Esters of phthalic, sebacic, adipic, maleic and other organic acids are mainly used as PVC plasticizers.

Dialkyl phthalate plasticizers occupy 70% of the plasticized PVC market in Russia, among them the most common general purpose plasticizer is dioctyl phthalate (DOP) [1, 2]. However, this plasticizer belongs to toxic products (hazard class 2), therefore, the possibility of its use in the production of materials and products in contact with medical and food products is limited. In this regard, there is an increasing need to use safer plasticizers in the production of polymeric materials [7–9, 10-23].

From this point of view, attention should be paid to its isomer - dioctyl terephthalate (DOTP), which is characterized by significantly lower toxicity, due to the location of ester groups in the para-position. According to some data, DOTP, unlike DOP with ester groups in the ortho position, does not turn into an active monoester [8, 24-31]. In addition, DOTP is highly compatible with PVC and has low volatility.

It is known that ester plasticizers at temperatures above 100°C, in the presence of oxygen, undergo oxidation, which is accompanied by the accumulation of hydroperoxide groups in the plasticizer, which have an accelerating effect on the process of polymer dehydrochlorination [1].

The presence of oxygen in the medium in which the process of polymer decomposition takes place leads to a change in the kinetic patterns of the degradation process, and is also accompanied by a change in the chemical structure of

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macrochains and the properties of the polymer. The thermal-oxidative decomposition of PVC, as well as the decomposition of many carbon chain polymers, is mainly considered as a free radical process activated by the interaction of oxygen with normal vinyl chloride units of the polymer, followed by the decomposition of the resulting hydroperoxides and the formation of free radicals that continue the kinetic chain [2].

The value of the rate of polymer dehydrochlorination in the presence of plasticizers of various natures correlates with their resistance to oxidation. In this regard, the kinetics of PVC degradation in the presence of oxygen depends mainly on the oxidative stability of the plasticizer, this factor is the main reason for the significant difference in the rates of decomposition of polymers with plasticizers of various nature [3, 4].

This paper presents comparative experimental results on the study of the process of thermal oxidation of DOTP and DOP plasticizers, as well as their influence on the rate of thermal oxidative dehydrochlorination and the thermal stability of PVC. Effective commercially available antioxidants have been selected to protect plasticizers.

Experimental part

The thermal stability of PVC-based compositions was evaluated by the "thermal stability time" indicator, which was determined by the time of the induction period of the color change of the "congo red" indicator during the release of HCl during the degradation of the polymer (175 °C and 190 °C) according to GOST 14041–91.

The process of accumulation of hydroperoxides during the thermal oxidation of DOP and DOTP plasticizers was studied by iodometric titration.

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The rate of PVC dehydrochlorination was determined during thermal exposure of polymer samples by the amount of released HCl by continuous dehydrochlorination in an oxygen flow (3.5 L/h).

The color of the plastic compound before and after heating at 180°C for 30 minutes was measured in the CIE Lab color space with an X-Rite spectrophotocolorimeter.

The performance characteristics of plasticized PVC materials were evaluated by standard methods.

Discussion of results

The results of studying the effect of DOP and DOTP plasticizers on the thermo-oxidative degradation of PVC in air at temperatures of 175 and 190 °C at a dosage of plasticizers from 0 to 40 wt. hours/100 wt. h.

With the introduction of plasticizers into PVC and an increase in their content, the rate of thermooxidative dehydrochlorination of the polymer increases, while the highest rate of polymer degradation is observed in the presence of DOP. PVC with DOTP plasticizer has a higher thermal and oxidative stability. Probably, this is facilitated by the location of ester groups in the para position. In [15], the mechanism of thermal oxidation of esters was studied. The authors found that the resulting hydroperoxides decompose into radicals, which, during the destruction of plasticized PVC, have an accelerating effect on the process of polymer dehydrochlorination.

In this regard, in order to inhibit the process of accumulation of hydroperoxides in plasticizers and increase the thermal-oxidative stability of PVC, the effect of commercially available non-toxic antioxidants - 2,6-di-tert-butyl-4-methylphenol (ionol), 4-hydroxy-3,5- di-tert-butylphenylpropionic acid (Irganox 1010).

As follows from the obtained experimental data, administration of the antioxidants Ionol and Irganox 1010 sharply inhibits the accumulation of hydroperoxides. Irganox 1010 is practically comparable to the antioxidant Ionol in

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terms of its inhibitory efficiency in relation to the thermal oxidation of esters. The optimal dosage of antioxidant in plasticizers, to achieve the maximum efficiency of the antioxidant action, is in the range of 0.3–0.5%.

The effectiveness of the use of the plasticizer DOTP in comparison with DOF was evaluated according to a number of technological and operational characteristics of the cable compound O-40 rec. OM-40.

Stabilization of plasticizers with ionol makes it possible to obtain a PVC compound with improved technological and operational characteristics, in particular, higher thermal stability and better retention of properties during heating and aging. Obviously, the antioxidant effectively protects the plasticizer from oxidation, which, in turn, increases the thermal stability of PVC due to solvation stabilization (the well-known effect of PVC "echo stabilization" [16]. The DOTP plasticizer provides a higher level of technological and operational properties.

Conclusion. Thus, on the basis of the conducted studies, it was found that the plasticizer DOTP is more resistant to oxidation and has a lesser effect on the thermal-oxidative degradation of PVC, in comparison with the widely used in the production of PVC plasticates DOP. The use of the DOTP plasticizer stabilized with antioxidants seems appropriate both to improve the color and thermal stability, durability of PVC compounds, and the need to solve economic and environmental problems.

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