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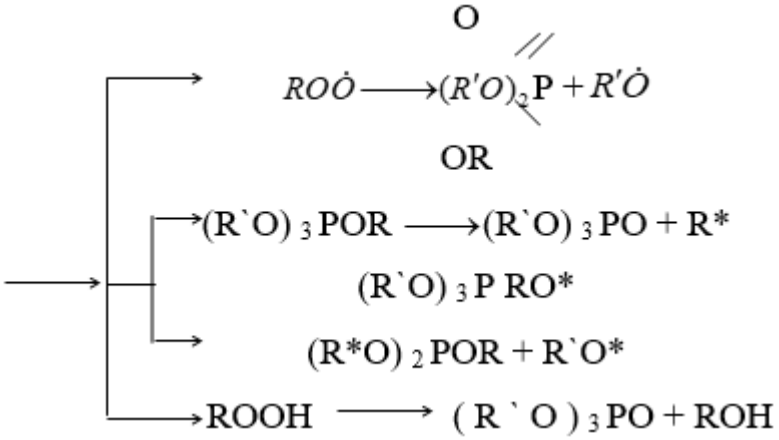
Stabilization of Polyvinyl Chloride

S.Sh.Lutfullaev
Professor of the Karshi State Technical University

Abstract: The article presents the results of analyzes carried out with different chemical compounds, which significantly slows down the harmful effect of oxygen under thermal decomposition of polyvinyl chloride. Comprehensive studies have shown that gossypol is a strong inhibitor of free radical oxidation and surpasses in efficiency many known synthetic inhibitors.

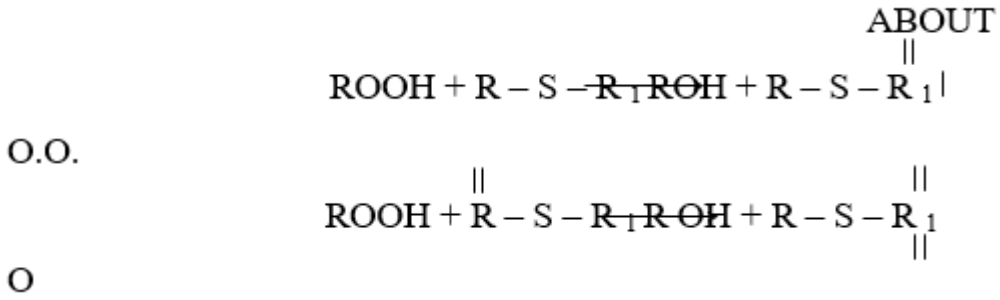
Keywords: Antioxidants, gossypol, gossypol hexamethyl ester, thermal degradation, Brabender - plastograph, □-furylacrylic and sorbic acid, zinc carboxylates, dimethyl-, tetramethyl-, hexamethyl esters of gossypol, aliphatic sulfides, metal-containing heat stabilizers.

Stabilization of thermal-oxidative decomposition of PVC is carried out by introducing organic additives - antioxidants capable of preventing or significantly slowing down the harmful effect of oxygen under conditions of thermal decomposition of the polymer. To protect polymers based on vinyl chloride and plasticizing additives from the oxidative action of atmospheric oxygen, phenolic stabilizers-antioxidants, organic phosphites and organic sulfur-containing compounds are widely used [1]. In addition to the listed compounds, other products have been proposed as antioxidants, which, however, as a rule, have no practical value in stabilizing PVC. Phenolic compounds are usually components of complex stabilizers and are used in combination with metal-containing PVC thermal stabilizers. Organic phosphites are widely used as antioxidants in PVC composites. Due to the presence in the structure of a highly reactive phosphorus atom, which contains unshared electron pairs and unfilled d- orbitals, phosphites effectively inhibit the oxidative decomposition of PVC. First of all, the inhibiting capacity of thermo-oxidative decomposition of PVC occurs due to the breaking of kinetic oxidation chains and without radical reduction of hydroperoxides:



Organic phosphites of the aliphatic series interact with hydroperoxides at significantly higher rates than aromatic ones. Organic compounds containing sulfur interact with hydroperoxide

groups as organic phosphites. Aliphatic sulfides have the greatest inhibitory effect than mixed ones, and aromatic sulfides do not react at all. When interacting with hydroperoxides, sulfides first transform into sulfoxides, and then into sulfones:



Individually sulfur-containing compounds are not used, since they are relatively ineffective. They are mainly used in combination with organic bases, metallic soaps and metal oxides. In the production of cottonseed oil, depending on the technological process and methods of isolating the main products, a secondary product is formed - gossypol - a natural phenolic antioxidant capable of inhibiting the processes of oxidative degradation of polymers. Gossypol and its derivatives are used as individual thermal stabilizers - antioxidants and studied to obtain a new class of stabilizers for a number of polymers PE, PP, PA, PVC, PVF, as well as general-purpose and special-purpose rubbers SKI, SKN, SKMS, SKF and others. Comprehensive studies have shown that gossypol is a strong inhibitor of free-radical oxidation and is superior in efficiency to many known synthetic inhibitors. Gossypol and derivatives based on it are inhibitors of oxidative decomposition, as well as thermal decomposition of polymers. Gossypol and its derivatives, such as anthranilate gossypol, increase the stability of a number of polymers under thermal oxidation conditions. These include rubbers obtained by polymerization using metal complex catalysts, where gossypol, along with its antioxidant action, reveals the function of a passivator for metals of variable valence. The high efficiency of gossypol is associated with the characteristic features of its chemical structure - the symmetry of the molecule and the presence of six hydroxyl groups participating in the inhibition of the radical reaction. Work in the field of polymer stabilization with gossypol and its derivatives has been carried out by many researchers, however, the patterns of the relationship between the inhibitory activity and the structure and the effect of the functional groups of gossypol on the polymer have not been studied. In [2], the effect of the functional groups of gossypol on the antioxidant activity of the polymer was studied. Isotactic polypropylene, which has been sufficiently studied in terms of inhibition by gossypol, was chosen for the study. To study the effect of gossypol functional groups on antioxidant activity, the issues of blocking gossypol hydroxyl groups were investigated and dimethyl, tetramethyl, hexamethyl ethers of gossypol and apogossypol with blocked aldehyde groups were used. The results of the study showed that with an increase in the blocking of hydroxyl groups, the inhibitory activity decreases, and the hexamethyl ether of gossypol exhibits the properties of an inert substance. Having compared the obtained data of the studied compounds, it was established that the aldehyde group of gossypol does not affect the antioxidant activity of polypropylene [3].

The effect of thermal stabilization of PVC by alkaline earth carbonates was studied using DTA. Samples containing magnesium carbonate, lead sulfate and their mixtures were subjected to dynamic thermal testing using a Burstoff roller and a Brabender plastograph. The results showed the stabilizing effect of these compounds obtained in non-isothermal experiments, and they can be used as additives in PVC processing.

The most widely used stabilizers in the production of PVC products are metal-containing stabilizers, epoxy compounds synthesized on the basis of synthetic fatty acids. These stabilizers have effective stabilizing properties in the production of PVC products. However, when using one stabilizer, a weak stabilizing effect is manifested. In addition, they are difficult to access, and most of them are expensive and toxic. These stabilizers are limited to acting in only one direction in relation to PVC stabilization. For example, they increase thermal stability, but do not affect its

thermal-oxidative decomposition. Cadmium stearates and laurates have found wide application as effective stabilizers of PVC compositions, which impart thermal stability and transparency to its products. The use of cadmium soaps as the only thermal stabilizers prevents a sharp blackening of the polymer containing them after short-term heat treatment. Cadmium soaps in combination with barium soaps lead to a significant synergistic effect in terms of thermal stability time and color fastness; Although a large number of individual cadmium stabilizers such as laurate, stearate and cadmium hexonate are produced, however, more widespread are complex cadmium-containing stabilizers (solid and liquid), containing additives of antioxidants, chelators, epoxy compounds, etc. Alkaline earth metal salts are also used α- furylacrylic and sorbic acids to ensure the preservation of the original color of PVC. The disadvantages of the above stabilizers are low thermal stability when used separately for PVC, a shortage of raw materials, as well as the toxicity of most of them. Zinc carboxylates are not used individually for PVC stabilization, since they have low thermal stability. They are usually used in combination with cadmium and barium soaps, epoxidized vegetable soaps, etc. In addition to the above compounds, sodium, potassium, lithium and barium stearates are used as thermal stabilizers of the HCl acceptor for PVC compositions. On their basis it is possible to obtain PVC plastisols with such special properties as transparency, weather resistance, etc. It should also be noted that many metal-containing compounds have a negative impact on hygienic working conditions if they enter the air in the form of dust.

Thus, research into chemical additives shows that certain work has been done in this area, which has made it possible to resolve some issues of targeted search for the most effective heat stabilizers.

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