

Influence study of thermostabilizers on the properties of cellulose triacetates

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Abstract. In the chemical and petrochemical industry, the primary focus for workers in the upcoming years is to develop innovative and secure technologies and equipment that comply with stringent quality standards. This imperative encompasses the production of materials, devices, and other products that meet the highest global benchmarks in technical and economic aspects. Emphasizing the implementation of progressive technologies and advanced production methods is crucial for achieving substantial improvements in labor productivity across all sectors of the national economy, with special attention paid to the chemical industry. This paper work presents the results of a study on increasing the thermal stability of cellulose triacetate by introducing stabilizers into its composition. Regularities of plasticization of cellulose triacetate with low- and high-molecular compounds have been established. As a result, the deterioration of the physical and mechanical properties of polymer materials processed at high temperatures occurs due to thermo-oxidative degradation, which leads to changes in the composition of the main polymer chain and a decrease in molecular weight. The application of stabilizers is proposed to prevent this process at high temperatures.

1. Introduction

The most important task for workers in the chemical and petrochemical industry in the coming years is the creation of safe new technologies and equipment that meet the required quality standards. This includes ensuring the production of materials, equipment, devices, and other products that meet the highest global standards in terms of technical and economic indicators [1]. Additionally, it involves the implementation of progressive technologies and advanced production methods to significantly increase labor productivity in all sectors of the national economy. This directive is of particular importance for the chemical industry [2].

To ensure technological progress in the chemical fiber industry, it is necessary to develop technological processes that would reduce the consumption of raw materials, energy resources, scarce materials, and water [3, 4]. The main goal is to transition major artificial and synthetic fiber enterprises to zero-discharge and waste-free technology. Special attention is given to the development of fibers with improved consumer and hygienic properties, which are used in the production of widely consumed goods [5, 6].

As known, triacetate fibers are formed by a dry method from solutions, in which the fibers are formed as a result of evaporation at an elevated temperature of the organic solvent methylene chloride from the streams of the solution flowing from the holes of the spinneret [7, 8].

Therefore, in terms of the above, the efficiency of triacetate fiber production can be significantly increased by replacing the dry forming method with melt spinning. With this forming method, production is made safer and more cost-effective by eliminating all operations related to spinning solutions (dissolution, filtration, deaeration) from the manufacturing process and eliminating the need for solvent capture.

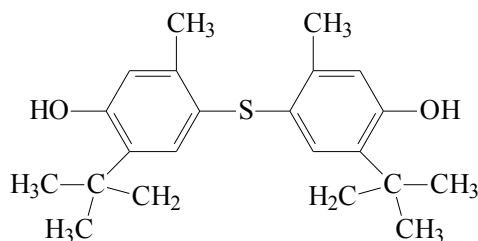
2. Materials and methods

The role of a thermal stabilizer is to absorb oxygen, bind hydrolytic agents, or interrupt chain reactions initiated by active radicals [9, 10]. Usually, phenol derivatives are used for the thermal stabilization of cellulose acetate-based products.

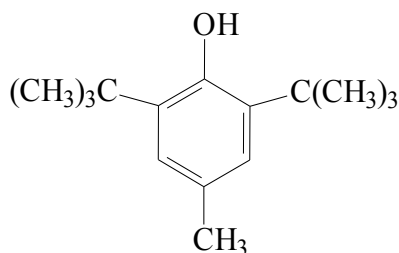
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Based on the foregoing, the following compounds were used as thermal stabilizers for triacetate cellulose (TAC) with an SP (saponification number) of 270 and a bound acetic acid content of 60.5%:

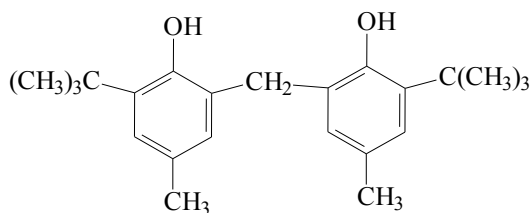
1. Bis - 2-hydroxy-5-methyl -3- tert-butyl -phenyl sulfide (CAO-b)



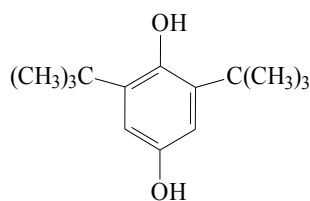
2. 4-methyl-2, 6-di-tert-butylphenol (alcophene BP)



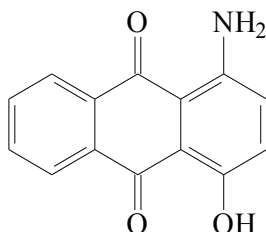
3. Bis-(2-hydroxy-5-methyl-3-tert-butylphenol)– methane(Angiooxidant-2246)



4. 2,5-di-tert-butylhydroquinone (debug)



5. 6-amino-9-exci-anthraquinone (disperse dye)



The mechanism of action of the above compounds is based on the fact that during the catalytic decomposition of hydroperoxides radicals $RO\cdot$ are formed and $RO_2\cdot$ being carriers of kinetic chains of oxidation.

The appearance of phenoxyl radicals in such systems modeling oxidation indicates the abstraction of the hydroxyl hydrogen of phenol by active radicals as the primary elementary act of inhibition, and the reactivity of the OH group in phenol is one of the most important characteristics of phenol as an inhibitor [3–7].

The heat-stabilizing abilities of these compounds were studied by changing the intrinsic viscosity and the amount of bound acetic acid in TAC. The objects of study were CTA films cast from a solution of cellulose triacetate with the addition of thermal stabilizers. To study their resistance to thermal oxidative degradation, films were placed on a chamber at 493, 523, 543 K for 600–1800s.

3. Results and discussion

Table 1 presents comparative data on the effect of different amounts of heat stabilizers on the molecular weight of cellulose triacetate exposed to high temperatures.

Table 1. Influence of the nature of stabilizers on the destruction of CTA films during heating for 600s.

Name of stabilizers	Quantity Stabilizer, % (by weight of TAC)	493 K		523 K		548 K	
		[η]	h.o., %	[η]	h.o., %	[η]	h.o., %
TAC parent Bis-2-hydroxy-5-methyl-3-tert-butyl-phenyl sulfide	0	1.6	57.9	1.39	57.6	1.1	49.3
(CaO-6)	0.5	1.70	60.0	1.56	58.5	1.48	57.4
(CaO-6)	1.0	1.64	59.4	1.54	58.1	1.32	50.0
Bis-2-hydroxy-5-methyl-3-tert-butyl-phenylmethane	0.5	1.65	60.0	1.56	58.4	1.45	51.3
Antioxidant-2246	1.0	1.70	60.5	1.65	60.0	1.56	58.5
2,5-di-tert-butyl-hydroquinone (dibug)	0.5	1.65	60.0	1.54	56.6	1.44	52.3
2,5-di-tert-butyl-hydroquinone (dibug)	1.0	1.65	60.1	1.58	59.4	1.42	52.0
4-methyl-2,6-ditertbutyl-phenol (alcophene BP)	0.5	1.65	60.0	1.50	57.2	1.4	51.0
4-methyl-2,6-ditertbutyl-phenol (alcophene BP)	1.0	1.65	59.4	1.45	50.0	1.39	51.5
Dispersed anthraquinone dye	0.5	1.65	60	1.60	58.4	1.49	51.7
Dispersed anthraquinone dye	1.0	1.70	60.5	1.70	60.0	1.65	58.5
x/y of the original TAC [η] = 1.70; n.o. = 60.5%.							

As can be seen from the data in Table 1, the inherent viscosity of cellulose triacetate without a stabilizer decreases from 1.70 to 1.1 at 600s exposure at a temperature of 543 K and at 0.38 when exposed to 493 K for 1800s (Figure 1). The introduction of thermal stabilizers leads to a decrease in the destructive effect of high temperatures. Thus,

at 548 K, the intrinsic viscosity of TAC with the addition of 0.5% SAO-6 and 1.0% antioxidant - 2246 is less, it changes than that of the original TAC. Similar results are observed when used as a heat stabilizer debuga (0.5 and 1.0% by weight of TAC). Antioxidant-2246 and anthraquinone dye in an amount of 1.0% (by weight of TAC), both at 523K and at 548K, have the greatest stabilizing ability (from 60.5 % To 58.5%), and for the original cellulose triacetate from 60.5 to 50.0%. Since the goal of our work was to obtain a thermostable CTA for spinning fibers from a melt, we studied its thermal stability at the melting temperature [8–10].

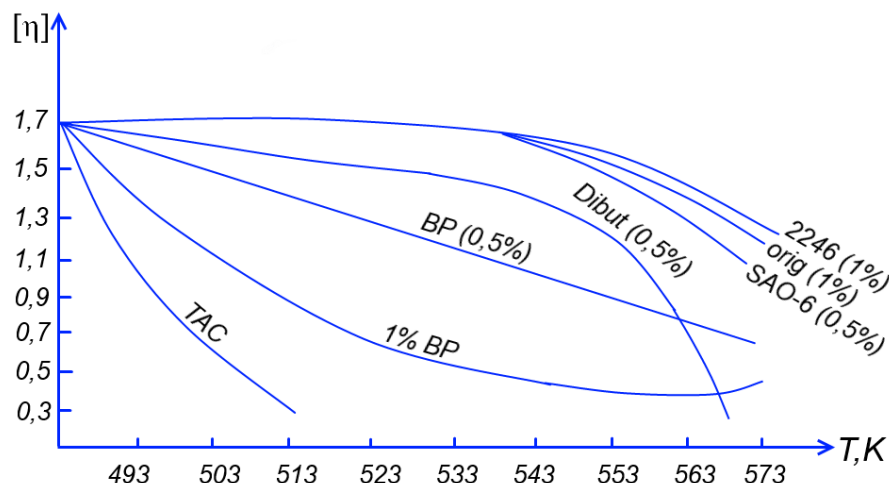


Fig. 1. Influence of the nature of stabilizers on the change in the intrinsic viscosity of CTC heated at different temperatures.

The thermal stability of the original TAC and with the addition of thermal stabilizers was checked by changing the specific viscosity of a 0.25% polymer melt solution in a methylene chloride -alcohol (9:1) mixture. For this purpose, melts of the indicated products were obtained in a special installation (LPUR). The results of the study are shown in Figure 2.

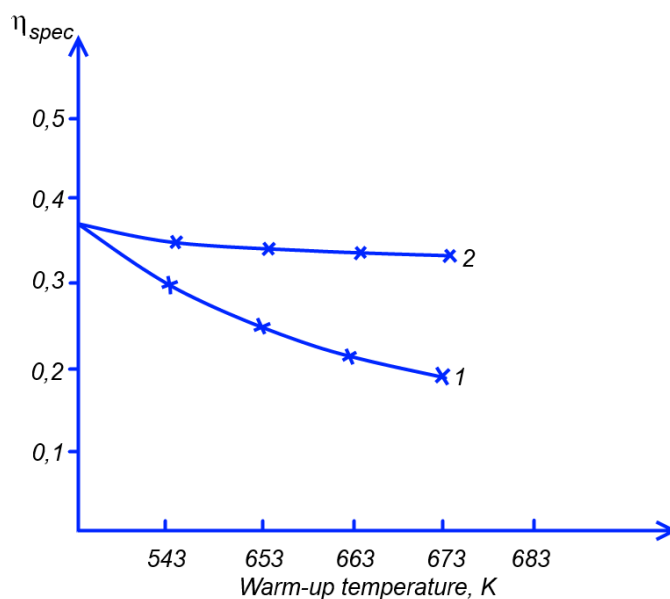


Fig. 2. Dependence of specific viscosity on original (1) and with a content of 1.0% antioxidant - 2246 (2) TAC during heating.

As can be seen from the data in Figure 2, when a polymer melt is obtained without a thermal stabilizer, with an increase in temperature, the specific viscosity decreases from 0.37 to 0.19. At the same time, when a polymer with a thermal stabilizer is melted, its specific viscosity decreases by only 13%. Similar results were obtained in the study of the physical and mechanical properties of cellulose triacetate films with the addition of other thermal stabilizers. The data are presented in Table 2.

It can be seen from Table 2 that the best polymer stabilization effect was obtained in the presence of antioxidant 2246 and anthraquinone dye in an amount of 1.0% (of the CTA chassis). At the same time, the physico-mechanical properties of the films remain at the level of films from the original CTA before heat treatment.

Based on the above index, in the future, as a stabilizer of thermo-oxidative destruction during the formation of triacetate eyelids, a curl from the melt, an antioxidant - 2246 and an anthraquinone dye were used. Tables 2 and 3 present data on spinning fibers from stabilized cellulose triacetate with antioxidant 2246 and anthraquinone dye.

Table 2. Influence of the nature and amount of the stabilizer on the physical and mechanical parameters, heat-treated for 10 pp. TSAT - X/Y films.

Name of the stabilizer	Quantity Stabilizer congestion, %	493 K		523 K		548 K	
		Breaking strength, N/mm ²	Elongation, %	Breaking strength, N/mm ²	Elongation, %	Breaking strength, N/mm ²	Elongation, %
Control	0	62.0	4.0	52.0 •	2.8	-	-
SAO - 6	0.5	81.0	6.4	81.0	5.5	73.0	4.8
Antioxidant -2246	1.0	82.0	6.5	82.0	5.8	75.0	5.1
Alcofen BP	0.5	78.0	5.8	70.0	5.4	60.0	3.6
Dibug	1.0	80.0	6.2	75.0	< 5.7	62.0	4.5
Dispersed Anthraquinone Dye	1.0	82.0	6.5	82.0	5.8	75.0	5.1
x / y of the original CTA film P \u003d 82.0 N / mm ² E = 6.6%							

Table 3. The effect of the amount of stabilizer on the non-chemical properties and the degree of destruction of CTA fibers (spinning temperature - 633 K, speed - 860 m/min, pressure - 3.2 MPa/.x/)

The amount of antioxidant 2245 in polyleast, %.	Joint venture	Tensile strength, cN/tex	Breaking elongation, %
0	185	17.2	14.8
0.5	220	17.3	15.1
0.7	235	17.5	15.0
1.0	240	17.8	15.9

As can be seen from Table 3, the introduction of the antioxidant - 2246 slows down the degradation process. This is expressed in a slight change in the SP TAC after molding. A sufficient amount of stabilizer is 0.7 - 1.0% of the cash register of cellulose triacetate.

As can be seen from Table 4, in the presence of a disperse dye, the smallest change in the SP of the polymer under the action of high temperature is observed. So CTA fiber after spinning without dye .have SP-185, and with the introduction of 1.5% dye in the TAC, the SP is £45. At the same time, the resulting dyed fiber has improved physical and mechanical properties, the strength is 18.4 cN /tex, and the elongation is 24.7%.

Table 4. Influence of the amount of dispersed anthraquinone dye on the properties of CTA fibers (T - 633 K, V - 440 m/min, P - 3.2 MPa).

Quantity dye, % (from the mass of the TAC)	joint venture	Tensile strength, P, cN/tex	Breaking elongation, %
ABOUT	185	14.5	14.0
0.5	210	16.8	18.4
1.0	220	16.0	26.0
1.2	230	16.8	28.5
1.5	245	18.4	24.7

Studies have shown that similar results can be obtained when used as a heat stabilizer dimethyl-bis-(p-phenylaminophenoxy)-silane (C-I) and it can be introduced during the production of cellulose triacetate. For this, acetylation of cellulose was carried out according to the usual method, using perchloric acid as a catalyst. At the end

of the esterification, an acetic acid solution of the stabilizer was added to the "syrup" in an amount of 0.2-1.0% of the weight of the original cellulose. Planting, washing and drying of the stabilized cellulose triacetate was carried out in the usual way. Cellulose triacetate, as a result of such stabilization, turned out to be colored orange. The effect of the stabilizer was checked by changing the degree of polymerization of cellulose acetate before and after heating at 433 K for 1800s (Figure 3).

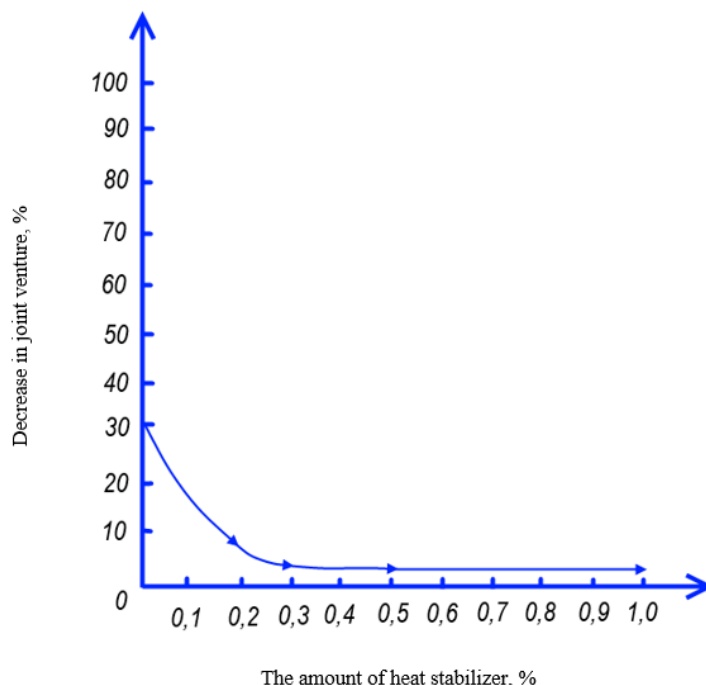


Fig. 3. Effect of the amount of stabilizer on the decrease in the SP of cellulose triacetate after heating at 463 K.

4 Conclusions

C-I is a very effective stabilizer, which ensures the preservation of almost the original degree of polymerization during heat treatment. It has been established that the addition of thermal stabilizers to CTA before heat treatment or in the course of its synthesis leads to a significant decrease in the degradation that occurs when it is operated at high temperatures.

Thus, for the first time, bicomponent fibers were formed from a melt using cellulose triacetate-synthetic polymer systems, such as acetopropionate, polystyrene, polycaprolactam, polyethylene terephthalate.

The structure and properties of the obtained fibers have been studied, and it has been shown that bicomponent fibers are superior in terms of physical and mechanical parameters to fibers based on CTA.

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