

Synthesis and Research of Thermostability of Stabilized Acrylic Emulsion for Finishing Dyeing in Leather Dressing

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ABSTRACT: The stabilized acrylic emulsion for finishing dyeing in leather dressing is synthesized and its thermal stability is investigated. The isothermal thermogravimetry of polymethacrylate and copolymers of methyl methacrylate with small amounts of thermal stabilizer revealed that samples of methyl methacrylate modified by links of the monomeric stabilizer had higher thermal stability than homopolymers of polymethacrylate. The greatest effect of thermal stabilization of polymers is observed when they contain 0.5-3.0 m.-% of links of a stabilizer, which demonstrates high effectiveness of the intramolecular stabilization. It is determined that values of activation energy of thermal-oxidative degradation are more for stabilized acrylic emulsion, than for not stabilized samples. The change in intrinsic viscosity of the solutions of stabilized and initial acrylic emulsions after destruction in the air shows that benzoxazoline fragments promote preservation of molecular weight of the modified acrylic emulsion, in comparison with the initial emulsion, the molecular weight of which decreases much faster. The increased stability of polymers at the first stages of degradation is explained by the availability of stable end groups, which are formed due to breaking of macroradicals at copolymerization. It is determined that with the increase of small amounts of new thermal stabilizing agent in the composition of acrylic emulsion and its presence in finishing polymeric composition in test variants, in comparison with control mixture, viscosity and modulus of elasticity increase to the defined value, and spreading capacity and elongation decrease. It demonstrates the great effectiveness of intramolecular stabilization of acrylic emulsion. A new polymeric composition on the basis of the stabilized acrylic emulsion has the increased physical-mechanical properties, including hygrothermal ones and resistance of coating to multiple bending of leather, water permeability decreases to 60,51 %.

KEY WORDS: Film forming, Polymerization, Copolymerization, Acrylic emulsion, 6-chlorine, 2-oxo, 3-benzoxazolilmethacrylate, Methacrylic acid, Acrylic acid, Casein, Shellac.

I. INTRODUCTION

Finishing dyeing of leather takes the central place among all cycle of dressing processes. Thus a grain is sleek and nice-looking and gets hydrophobic. Besides it is necessary to note that the traditional leather dressing with application of polyacrylic filmforming agents in coating compositions does not meet some use requirements.

The research in the field of monomer synthesis with stabilizing fragments of copolymerization for the purpose of creating self-stabilizing polymeric systems for finishing dyeing in the leather dressing process is of great scientific-theoretical and practical interest.

Now special additives, in particular low-molecular stabilizers, introduced into polymer immediately during processing are widely used for prolongation of polymeric materials and products lifetime. Low-molecular stabilizing additives have a number of lacks, such as migration, washing out, volatility, extraction by solvents, which frequently leads to the irrational consumption of stabilizers and deterioration of finished products. Over the last years interest in study of

thermal stability of coating on leather has increased in connection with wide application of hot cure of polyurethane soles to shoe upper in the shoe production.

Low thermal stability of polyacrylic coatings at high temperatures generates a need to restore grain damage.

Various synthetic film forming agents are usually used for finishing dyeing of leather [1]. Polyacrylates have the following positive properties. They are uncolored, elastic and hydrophobic. However, they have poor thermal stability and mechanical strength.

One of the major problems, which faces researchers in the field of high-molecular compounds, is to increase thermal resistance of polymers to various effects and forecast the lifetime of materials and products in application conditions [1].

It is very difficult to solve this problem because of the large variety of features of structure and properties of macromolecules, as well as application conditions of polymeric materials [2-4].

The inclusion of stabilizer molecules in macromolecular chains of polymer allows to vary additive distribution and to avoid its losses at processing and operation, and thus enables to prolong stabilizing action of the polymer.

As the statements indicates the research of thermal stability of acrylic emulsion (AE), frequently used in leather dressing, stabilized by monomer 6-chlorine, 2-oxo, 3-benzoxazolilmethylemethacrylate (6-Cl, BOMMA) obtained in the presence of reductive-oxidative initiators is of great interest [5].

II. METHODOLOGY

Initial materials

Methacrylic acid - grade "P" was distilled over copper chips for purification at atmospheric pressure, fraction boiling was run off at 163 °C, $n_D^{20}=1,4314$.

Acrylic acid - grade "P" was distilled over copper chips at atmospheric pressure, fraction boiling was run off at 141 °C [6].

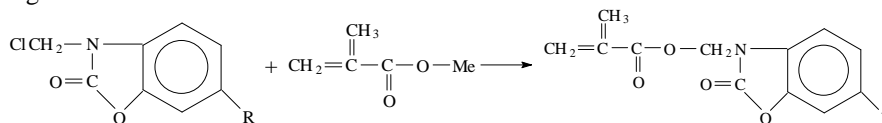
Sodium acrylates and methacrylates were synthesized according to a procedure [6]: Immediately after distillation acrylic or methacrylic acids were slowly added to cooled concentrated solution NaOH in methanol or ethanol to a neutral reaction. Then small excess of acid (10 %) was introduced, salt was precipitated with acetone or ether and filtered. After repeated dissolution in methanol and reprecipitation with ether, salt was washed with ether and acetone and dried in vacuum; salts decompose at above 220 °C, unsaturation (by bromine) - 93,2-99,4 %.

Benzoxazolinon industrial - solid powdery substance of dirty-white color was purified by boiling in water solution in the presence of activated carbon. $T_{\text{melt}}=141-142$ °C.

Methods

Methods for obtaining thermostabilizer 6-Cl, BOMMA

Reaction of obtaining monomer-stabilizer



where, R= Cl, H; Me = Na, K

6-Chlorine-benzoxazolinon was obtained according to a procedure [8]. 13,88 g (0,195 mole) of chlorine were passed through to mixture of 20,2 g (0,15 mole) benzoxazolinon-2 and 0,02 g (0,00036 mole) of iron in 100 ml of dichloroethane at 65-75 °C and stirring. The sediment was separated, washed with 10 ml of dichloroethane and dried.

22,8 g of 6-chlorine, benzoxazolinon-2 were obtained. The yield was 90%. $T_{\text{m}} = 190,5-191,5^{\circ}\text{C}$ (from ethanol). It is a solid powdery substance of light grey color, practically not soluble in water.

N-hydroxymethylbenzoxazolinon was synthesized according to a procedure [9]: 135 g of powdery benzoxazolinon were boiled (85°C) in 250 ml of water, then mixed with 14 ml of 33 % formalin to full dissolution of benzoxazolinon-2. The hot solution was immediately filtered and maintained at room temperature for 20 hours. The crystals, which had formed, were drawn off using Buchner funnel and washed with water several times. The yield was 82 %. $T_{\text{m}} = 110^{\circ}\text{C}$.

N-chlorine-methylbenzoxazolinon was obtained according to a procedure [10]. 4,95 g of finely ground N-hydroxymethylbenzoxazolinon and 45 % hydrochloric acid were stirred and heated for 10 minutes. The mass, which had formed, was filtered, washed with cool water to neutral medium. The yield was 5,0 g (91 %). $T_{\text{m}} = 203^{\circ}\text{C}$.

6-chlorine, 3-hydroxymethylbenzoxazolinon-2 and **6-chlorine, 3-methylbenzoxazolinon-2** were synthesized according to a procedure [9]. 6-chlorine, 3-methylbenzoxazolinon-2 is a solid powdery substance of light grey color, practically not soluble in water. $T_{\text{m}} = 117-118^{\circ}\text{C}$.

6-chlorine-2-oxo-3-benzoxazolinemethylmethacrylate (6-Cl, BOMMA) was obtained according to a procedure similar to that of BOMMA synthesis, by means of interaction of 3-chloromethylbenzoxazolinonil with alkali salts of (meth)acrylic acid. Reaction time made up 90 minutes at $50-56^{\circ}\text{C}$. Purification was carried out by recrystallization from the mix acetone : water (5:3). The yield was 88-90 %. $T_{\text{m}} = 90-91^{\circ}\text{C}$.

Method for obtaining heat stabilized acrylic emulsion

242,5 cm³ of water were poured in three-necked flask, than at mixer rotation 1 g of emulsifying agent C-10 diluted in 50cm³ of water, 5 g of dibutyl phthalate as plasticizer and 0,3 g of 25 % ammonia water were sequentially added. After 15 minutes of stirring, 100 g of methylacrylate were introduced and heating was started. 0,5-3,0 m.-% of 6-Cl, BOMMA were introduced into the reaction mixture simultaneously with dibutyl phthalate.

Initiators - 0,1 g of ammonium persulphate in 5 cm³ of water and 0,05 g sodium metabisulphite in 2,5 g of water - were introduced into the reaction mixture separately and by parts. The first portion (half) of initiators was introduced after 40-50 minutes from the beginning of the process when the temperature of the mix has reached $35-40^{\circ}\text{C}$ and the process of polymerization began. When the temperature has reached $62-65^{\circ}\text{C}$, the second half of initiators was added.

Polymerization was continued at $80-85^{\circ}\text{C}$ within 30-45 minutes. The end of the process was controlled by content of dry residue, which should be no less than 20 %.

Physical-chemical properties

The composition and structure of monomers are confirmed by the results of the element analysis, PMR-, UV-, IR-and mass- spectroscopy.

Table 1. Physical-chemical constants of monomer-stabilizer (6-Cl,) BOMMA

Compound		BOMMA	6-Cl, BOMMA
Brutto-formula		$\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}$	$\text{C}_{12}\text{H}_{11}\text{O}_4\text{NCl}$
$T_{\text{m}}^{\circ}\text{C}$		86-87	90-91
Contents: %	C	61,80/61,16	53,83/53,34
	H	4,72/4,03	3,74/3,13
	N	6,01/6,11	5,23/5,02
	Cl	-	13,27/13,14

Note: Numerical values are given in numerator, obtained values - in denominator

The thermostabilizers (6-Cl), BOMMA obtained are colourless crystal substances, well soluble in acetone, benzol, dioxane, dimethyl formamide, dimethyl sulfoxide, badly soluble in spirits, not soluble in water.

The acrylic emulsion obtained had 40-42 % of dry residue with pH 5,4-5,8 that was resistant to the action of electrolytes and did not coagulate with ammonia. Surface tension was 38-42 m/ Nm, tensile strength - 8,9-9,4 MPa and elongation at rupture - 320-360 %.

Method for study of thermal degradation kinetics

Thermal degradation kinetics of the acrylic emulsion was studied by the isothermal and thermogravimetric methods. A modified Mac-Ben spring balance [11] was used. The sensitivity of a spring made of $25 \cdot 10^{-3}$ mm wolfram wire was 14,6 mg/m. Spring elongation was determined with a cathetometer KM-8, allowing to carry out measurements with accuracy of 100^{-5} m. The temperature of medium was held with accuracy of $\pm 2^{\circ}\text{C}$ and controlled by means of a potentiometer PP-63 with application of chromel-capel thermocouples.

III. RESULTS AND DISCUSSION

It is known that acrylic emulsion N1 is a product of methyl methacrylate (MMA) polymerization and in this connection MMA thermal properties have been investigated.

Isothermal thermogravimetries of polymethacrylate (PMMA) and MMA copolymers with small amounts of 6-Cl, BOMMA have shown that MMA samples modified by links of monomer stabilizer have higher thermal stability than PMMA_homopolymers. Besides, the greatest effect of thermal stabilization of polymers is observed when they content 0,5-3,0 m.-% of 6-Cl, BOMMA links, which demonstrates high effectiveness of intramolecular stabilization.

The intramolecular decomposition of initial AE and AE stabilized by 6-Cl, BOMMA at a predetermined temperature proceeds with constant reduction of mass loss rate in time, the greatest degradation rate of copolymers takes place at the initial stage of the process. Then it changes insignificantly. In all cases mass loss in the air is more than that in vacuum, which is probably connected with influence of atmospheric oxygen. It promotes the formation of peroxides and hydroperoxides, which further decompose and initiate the process of thermal-oxidative degradation.

Thermal stability of copolymers was also evaluated by the method of differential-thermal analysis.

As shown in (Fig. 1), AE copolymer on the basis of MMA with small contents of 6-Cl, BOMMA has higher thermal stability compared to the initial AE.

Kinetic curves of thermogravimetry of the stabilized and initial AE have S-shaped character. It means, that the mass of films being investigated slowly decreases at the beginning of degradation, and then quickly increases in rather narrow interval of temperature range. In [Poomalai, Varghese, and Siddaramaiah](#) opinion [12] it is caused by accumulation of structures with end unsaturated groupings in copolymers.

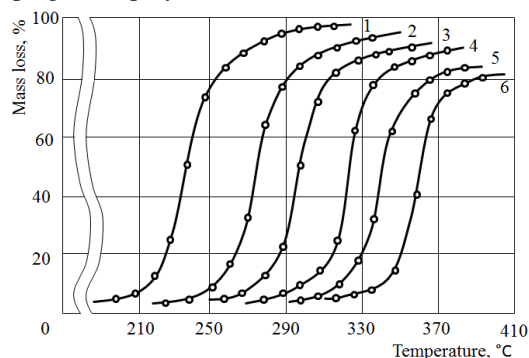
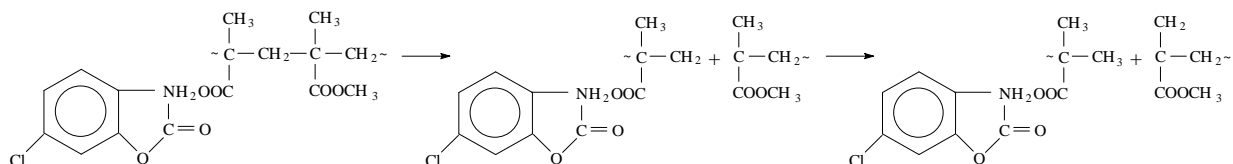


Fig 1: Dependence of mass loss of initial AE N1 and AE stabilized with 2- 0,5; 3-1,0; 4-2,0; 5-3,0 and 6-4,0 m.-% of 6-Cl, BOMMA at heating in the air. Heat rate – $5^{\circ}\text{C}/\text{min}$.

It is probably connected with random decompositions of copolymers macromolecular chains in which bond strength decreases at high temperatures. Thus the disproportionation reaction can proceed by the schema:



The end double links formed with growth of temperature of thermal-oxidative decomposition promote increase of depolymerization rate.

As is known oxidation of polymers is accompanied by degradation processes, which result in reduction of their molecular weight and degradation of physical-mechanical characteristics. The initial temperature of decomposition of copolymers, compared to that of unstabilized AE, is shifted in the area of higher temperatures, which allows to make a conclusion about the great effectiveness of intramolecular stabilization of the initial AE.

Table 2 presents parameters of thermal-oxidative degradation of stabilized samples of AE films in the air at heating rate of 5°C/min.

Table 2. Parameters of thermal-oxidative degradation of chemically stabilized samples of AE films in the air

System	Unstabilized AE	AE stabilized with 6-Cl, BOMMA				
Contents of stabilizer, m.-%	-	0,5	1,0	2,0	3,0	4,0
Temperature of decomposition starting, °C	210	240	270	290	310	340
Temperature of maximum mass loss rate, °C	310	330	350	370	380	390
Maximum mass loss at 310 °C, %	97	86	75	72	68	54
Energy of thermal-oxidative degradation, kJ/mole	190±1,2	194±1,3	211±1,2	239±2,1	242±1,3	244±2,1
Degree of viscosity conservation, %	84,51	86,07	80,26	75,14	71,82	69,44

As can be seen, the values of activation energy of thermal-oxidative degradation for the stabilized AE are higher than that for unstabilized samples. The change in intrinsic viscosity of solutions of the stabilized AE and the initial AE after degradation in the air indicates that benzoxazoline fragments promote conservation of molecular weight of the modified AE, in comparison with the initial one at which it decreases much faster. It is probably connected with blocking of polymer end groups by monomer-stabilizer molecules in chain transfer acts during the process of copolymer formation. Therefore the increased stability of polymers at the first stage of degradation (195 °C) can be explained by availability of stable end groups which are formed due to detachment of macroradicals during copolymerization. At temperature of more than 195°C, when the nature of end groups does not play an essential role, initiation of decomposition occurs by the law of chance, i.e., noticeable distinction in degradation rate of all stabilized copolymers is not observed.

Control and test compositions were prepared for study of stabilized AE behavior in finishing dyeing of leathers.

The polymeric composition of control variant 1 was made according to a formula [13] with use of the unstabilized AE. Compositions of test variants 2-6 were prepared on the basis of the stabilized AE with 6-Cl, BOMMA in various initial ratios.

Compositions for finishing dyeing of leather are given in Table 3.

Table 3. Compositions of control and test variants for finishing dyeing of leather, in parties by mass

Composition	Variants							
	Control	Test						
	1	2	3	4	5	6	7	8
Pigment concentrate: on nigrosine basis	80	80	80	80	80	80	80	80
on black basis	20	20	20	20	20	20	20	20
10% casein	50	50	50	50	50	50	50	50
10% shellac	50	50	50	50	50	50	50	50
20% AE №1	100	-	-	-	-	-	-	-
20% AE №1 stabilized with 6-Cl, BOMMA	-	50	70	80	90	100	120	130
20% wax emulsion	10	10	10	10	10	10	10	10
20% dispersion MX-30	100	100	100	100	100	100	100	100
Latex DMMA-65 GP	100	100	100	100	100	100	100	100
Water	160	160	160	160	160	160	160	160

Polymeric compositions for finishing were homogeneous on all mass: homogeneous black color, viscous, with dry residue of 19,74-23,81%.

Then their physical and chemical properties were investigated. Table 4 gives physical-chemical indicators of traditional control finishing composition and test finishing composition on the basis of the stabilized AE.

Table 4 shows that with the increase of small amounts of 6-Cl, BOMMA in the AE composition and its presence in finishing polymeric composition in test variants 2-6, in comparison with control variant 1, viscosity and modulus of elasticity increase up to defined value, and spreading capacity and elongation decrease. It is probably also connected with the great effectiveness of intramolecular stabilization of AE.

The increase of viscosity in test variants 3-8 with the stabilized AE can be explained by participation of 6-Cl, BOMMA in chain transfer acts in process of copolymerization with EA.

Then test and control polymeric compositions for finishing dyeing of leather were applied 4 times on samples of chrome-tanned leathers with the subsequent predrying.

Table 4. Physical-chemical indicators of traditional control finishing composition and test finishing composition on the basis of stabilized AE

Indicators	Variants							
	Con-trol	Test						
	1	2	3	4	5	6	7	8
Contents, in %								
-dry residue	19,74	20,13	22,92	23,38	23,42	23,63	23,72	23,81
-fat	1,63	1,60	1,57	1,53	1,53	1,53	1,52	1,52
-ash	1,63	1,60	1,57	1,53	1,53	1,53	1,52	1,52
Viscosity, Pa·s	4,6	4,5	5,1	5,8	5,8	5,8	5,8	5,9
Spreading capacity, g/m ²	75	64	52	46	46	46	45	45
Modulus of elasticity, 9,8 MPa	1,66	2,25	2,26	2,28	2,28	2,29	2,29	2,29
Elongation at rupture, %	65,5	64,6	63,7	62,4	61,9	61,9	61,8	61,8
Electrolyte stability per 10 ml of paint:								
0,3 ml of NaCl		not coagulated						
0,3 ml of (NH ₄) ₂ OH-25%		not coagulated						
0,3 ml of CH ₃ COOH		coagulated						

The consumption of finishing dye for all variants made up 46,5±0,2 g/m². Pressing was carried out on hydraulic press "Svit" at 90 °C and pressure of 15 MPa for 5 seconds.

The physical-mechanical properties of ready leathers were investigated after their finishing dyeing with use of the control and test compositions. The results are given in Table 5.

Table 5. Physical-mechanical properties of leathers covered with compositions of control and test variants

Variants	Indicators							
Test	Tensile strength, 9,8 MPa	Elongation at stress, 9,8 MPa, %	Stress at appearance of chaps on grain, 9,8 MPa	Vapor permeability, %	Hygrothermal stability, %	Wet abrasion resistance, in turns	Resistance of coating to multiple bending, marks	Water permeability, ml/cm ² h
Control 1	16,8	24,6	32,4	56,4	105,0	82,4	3	5,42
2	16,2	24,0	32,2	55,3	104,3	81,9	3	5,18
3	17,8	24,5	32,6	55,7	105,2	82,6	3	4,15
4	18,3	25,3	33,3	56,9	106,1	83,9	5	3,28
5	18,9	26,2	40,0	61,1	106,4	84,8	5	3,76
6	18,9	26,2	40,0	61,9	106,5	84,8	5	3,78
7	18,9	26,3	40,1	62,0	106,6	84,9	5	3,82
8	19,0	26,3	40,1	62,0	106,6	84,9	5	3,84
Test methods GOST	938.11			938.17	938-28	13869	13868	1821
Standards	No less than 10,0	20-40	No less than 10,0	20-70	No less than 70,0	No less than 50,0	No less than 2,0	No more than 10,0

The obtained results have shown that test samples covered with new polymeric composition on the basis of stabilized AE with 6-Cl, BOMMA have increased physical-mechanical properties, including hygrothermal ones and resistance of coating to multiple bending of leathers, and their water permeability decreases up to 60,51 %.

IV. CONCLUSIONS

Thus in process of emulsion copolymerization introduction of small amounts (0,5-3,0 mass. %) of monomer-stabilizer 6-Cl, BOMMA in the main chain of MMA raises the total reaction rate of copolymerization and reduces viscosity of copolymer solutions owing to participation of benzoxazole groups in a chain transfer reaction, and thereby thermal degradation of end product retards.

It has been revealed that copolymerization of the basic monomer with a small amount of monomer-stabilizer, i.e. the monomer containing stabilizing fragments in its structure, ensured the effective chemical stabilization. This leads to resistance of filmforming agents to ageing, improves quality of a coating film of ready leathers and prolongs their service life.

It has been determined that in order to increase the action of AE used in the composition for finishing dyeing it is necessary to stabilize it with a monomer 6-Cl, BOMMA. It has been established that stabilization of AE, which was a component of finishing dye, caused thermostable and strong structure of a composition, uniform distribution on grain, further resulting in mechanical properties of ready leather.

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