ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 11, pp. 2320–2324. © Pleiades Publishing, Ltd., 2014.
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Polyacrylamide in the Technologies of Utilization of Nitrocellulose Manufacturing Wastes

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Received January 1, 2013

Abstract—The article analyzes the use of polyacrylamide at various stages of utilization of nitrocellulose manufacturing wastes. The introduction of polyacrylamide as a flocculant in the process of treatment of nitrocellulose manufacturing wastewaters allows their purification to the level of drinking water quality. Parameters of the gel formation process of the compositions under study, which prevent filler sedimentation and stratification of the system, have been determined.

DOI: 10.1134/S1070363214110528

INTRODUCTON

Polyacrylamide and its anionic and cationic derivatives are among the most accessible, fairly cheap, and low-toxicity water-soluble polymers. Polyacrylamide has found diverse industrial applications, specifically as a flocculating agent in the technologies of natural and wastewater treatment, concentration and dewatering of mineral suspensions, stabilization of mineral suspensions on well drilling, manufacture of paper, paints, and plastics, as well as prevention of the formation of insoluble substances on the surface of chemical and heat-exchange equipment [1–3].

The broad application of polyacrylamide is explained by its ability to destabilize disperse systems. Polyacrylamide is a macromolecular polyelectrolyte which dissociates in water to form on its thread-like molecules charged centers which can attract suspended solid particles containing polyvalent metals on their surface. Polyacrylamide molecules form floccules favoring faster particle precipitation [4–7].

Polyacrylamide is included into various gel systems [8–10] that are used, in particular, for enhanced oil recovery [11].

The efficiency of polyacrylamide in gel-forming systems is maintained over a fairly wide pH range [4]. At the same time, the efficiency of such systems also depends on a number of other factors. As mentioned in [11], when dealing with gel-forming systems, one should take into account the composition and chemical compatibility of reagents and fillers used together with them, as well as conditions of preparation and application.

The focus of the present paper is the use of acrylamide (co)polymers for intensification of flocculation and gel-formation processes in the technologies of nitrocellulose manufacturing waste utilization or, more specifically, the choice of operating conditions for the nitrocellulose manufacturing wastewater treatment process, where polyacrylamide acts a universal flocculating and gel-forming agent.

Flocculation of Wastewater Generated in Nitrocellulose Production

Coagulation and flocculation are physicochemical methods used in industrial wastewater treatment. The most common coagulants are aluminum and iron(III) salts which hydrolyze to form sparingly soluble hydroxides $Al(OH)_3$ and $Fe(OH)_3$ [12–15]. These products neutralize negatively charged colloid particles in water, thus favoring aggregation of pollutant particles and their precipitation. The addition of a flocculant after a coagulant serves for fast formation of large flakes and increases the density of the coagulate and

the clarity of water. Flocculant macromolecules simultaneously adsorbed on two or several dispersed particles and bind the latter into aggregates by polymer bridges, thus destabilizing the disperse system [4, 6].

The size and density of flakes and the efficiency of the flocculation process as a whole depend on the intensity and duration of mixing. Mixing allows more uniform distribution of macromolecules in the bulk of water being treated, binding of a greater number of polymer chain segments to a greater number of particles, shortening of polymer bridges, and destruction of aggregates with shortened bridges. Therefore, the mixing speed should be such that large and dense flakes are formed but not destroyed.

Thus, joint use of coagulants and flocculants makes possible more efficient separation of wastewater from sedimented particles.

We proposed a Praestol 2510N polyacrylamide (Ashlend-MSP, Perm) to be used together with an aluminum sulfate coagulant in nitrocellulose manufacturing wastewater treatment.

In the experimental assessment of the efficiency of this treatment technology we used wastewater samples with the pH and turbidity corresponding to wastewater generated in nitrocellulose manufacturing (Table 1). Aqueous aluminum sulfate (3% or 6% solutions) was added under mixing until the coagulant has completely mixed with water (2 min). The polyacrylamide flocculant (1% or 0.5% aqueous solution) was added to water being treated 2 min after coagulant treatment. This time gap is required for more uniform distribution of the coagulant in water, its hydrolysis, and formation of primary particles. After polyacrylamide has been added, flakes formed in the turbid water get larger and denser.

Turbidity measurements were performed on a KFK-2 photocolorimeter with a green light filter (λ = 540 nm) in 5-cm cells. The turbidity of the samples was determined from the calibration curves obtained using solutions obtained by diluting a formazin stock solution.

The measurement results were expressed in mg/dm^3 and related to a kaolin standard suspension. Recalculation to the kaolin standard was performed using the following relationship: 1.5 mg/dm^3 kaolin corresponds to 2.6 turbidity units/dm^3 formazin.

The results of treatment of model samples of nitrocellulose manufacturing wastewater are shown in Fig. 1.

Table 1. Characteristics of the model samples of nitrocellulose manufacturing wastewater

Sample no.	pH of raw wastewater	Turbidity of raw wastewater, mg/dm^3
I	2	5.5
II	7	4.5
III	6	30.0

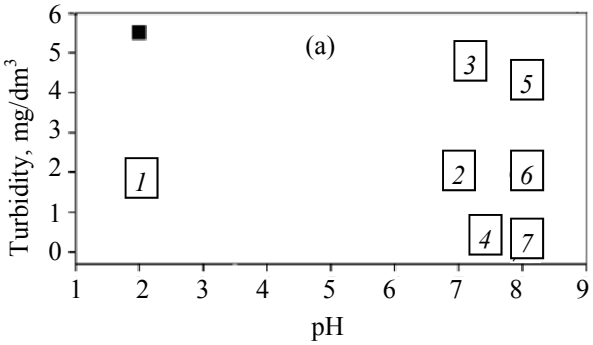
As seen from Fig. 1a, the flocculating power of polyacrylamide in the treatment of nitrocellulose manufacturing wastewater (sample I) depends not only on the pH of the medium (point *1*), which can be explained by the amphoteric nature of aluminum hydroxide and its low solubility in water at pH < 4 [16], but also on the relative quantities of the coagulant and flocculant (points *2, 3, 5*, and *6*). In the case of sample II (Fig. 1b), when the pH of the raw wastewater is close to normal, by varying treatment conditions one can reach a higher degree of purification (points *3* and *5*). With the raw wastewater *5* times as turbid as the other ones (sample III), the same regularities are observed (Fig. 1c).

It was thus shown that nitrocellulose manufacturing wastewater can be purified so that its pollution level meets the standard (maximum allowable concentration, MAC) for drinking water by successive treatment with a coagulant, specifically aluminum sulfate (3% or 6% aqueous solution) and a flocculant, specifically polyacrylamide (1% or 0.5% aqueous solution).

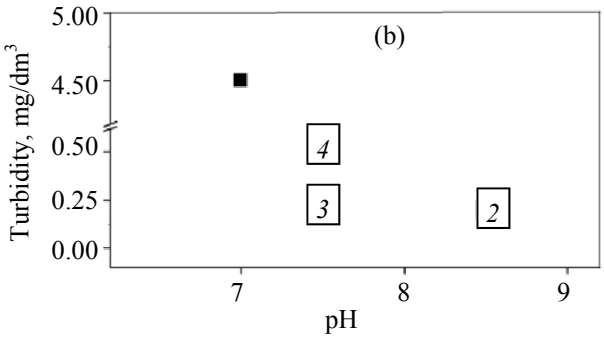
Utilization of the Entrapped Intermediate Product of Nitrocellulose Manufacturing

Utilization of nitrocellulose manufacturing wastes, specifically "trap" colloxylin, is quite an urgent problem in the context of provision of environmental and chemical safety of defense industrial facilities [17–20]. "Trap" colloxylin which is stored in traps and occupies large areas in industrial sites and a lot of equipment can be used as an energy thickening additive in explosive manufacturing industry. This approach seems to be the most rational way to utilize cellulose nitrate manufacturing wastes [21–25].

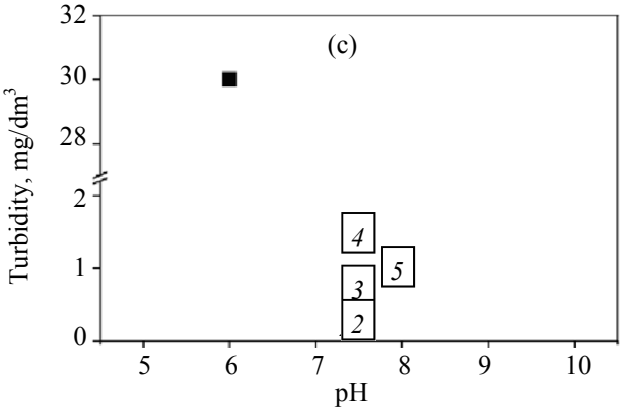
One of the types of industrial explosives is represented by water–gel explosives containing as gel-forming agents water-swelling synthetic or natural polymers, such as certain plant polysaccharides (guar



Point no.	pH	$Al_2(SO_4)_3$, mg/dm^3	PAA, mg/dm^3	Turbidity, mg/dm^3
1	2.0	0.300	0.06	2.0
2	7.0	0.300	0.06	2.0
3	7.2	0.060	0.06	5.0
4	7.5	0.300	0.06	0.5
5	8.0	0.150	0.06	4.5
6	8.0	0.084	0.06	2.0
7	8.0	0.048	0.06	0.0



Point no.	pH	$Al_2(SO_4)_3$, mg/dm^3	PAA, mg/dm^3	Turbidity, mg/dm^3
1	7.5	0.3	0.006	0.50
2	7.5	0.3	0.003	0.55
3	7.5	0.6	0.006	0.25
4	7.5	0.6	0.003	0.50
5	8.5	0.3	0.006	0.20



Point no.	pH	$Al_2(SO_4)_3$, mg/dm^3	PAA, mg/dm^3	Turbidity, mg/dm^3
1	7.5	0.3	0.006	0.25
2	7.5	0.3	0.003	0.25
3	7.5	0.6	0.006	0.50
4	7.5	0.6	0.003	1.50
5	8.5	0.3	0.006	1.00

Fig. 1. Turbidity of water before and after treatment of samples (a) I, (b) II, and (c) III with the use of the $Al_2(SO_4)_3$ coagulant and polyacrylamidea (PAA) flocculant. (■) Turbidity before treatment.

Table 2. Composition of the aqueous explosive composition

Component	Concentration, %
"Trap" nitrocellulose (active filler)	49.8
Ammonium nitrate	17.4–17.6
Diethylene glycol (cryogenic additive)	12
Water	20
Praestol 2510 polyacrylamide	0.6–0.8 (3–4% with respect to water)
$K_2Cr_2O_7$ and Na_2SO_3 (hardeners)	0.08

gum), salts of carboxymethylcellulose, polyacrylamide, etc. The water gels containing these components prevent or retard washing-out of ammonium nitrate and other water-soluble salts, as well as nitrocellulose in wet hole loading, endow industrial explosives with plasticity, adhesiveness, and other useful performance characteristics. The requirements to thickening agents depend on the explosive manufacturing technology [26]. In choosing the thickening additive to an explosive much attention is paid to the rate of gel formation. Gel formation is responsible for the rheological characteristics of the intermediate and final products. The viscoelastic properties of these products are the main issue taken into account in choosing instrumentation and optimal conditions for the implementation of the gel-formation process [23–25].

We performed a study of the rheological properties of aqueous explosive compositions on the basis of nitrocellulose manufacturing wastes. For the thickening agent we used a Praestol 2510N polyacrylamide. Gel formation in the system was induced by a redox reaction (potassium dichromate and sodium sulfite). The concentration limits of gel formation, i.e. the minimum concentrations of polyacrylamide and the cross-linking system, were determined visually by the self-gravity-induced loss of solution fluidity. The aqueous explosive compositions were prepared in laboratory conditions without evacuation in a batch mixer with an MR-25 stirrer drive at 18–25°C; the stirrer speed was 200 rpm. The compositions (Table 2) contained different concentrations of hardening components.

The rheological characteristics of the compositions were measured using a Rheotest-2.1 rotary viscometer (Medingen, Germany) with a cylinder–cylinder measuring system in the temperature range 30–40°C. The viscosities were measured at shear rates from 1 to 27 s^{-1}.

As seen from the dependence in Fig. 2, efficient hardening is observed at 30°C and hardening agent concentrations of 0.045% $K_2Cr_2O_7$ and 0.035%

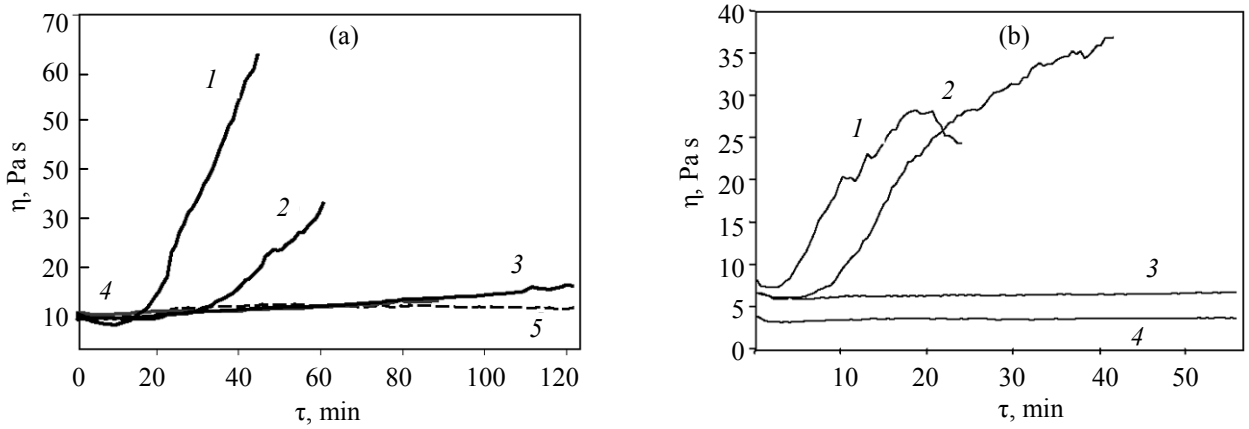


Fig. 2. Changes in the viscosity of aqueous explosive compositions with time at varied contents of hardeners: (a) (*1*) 0.05% $K_2Cr_2O_7$, 0.04% Na_2SO_3; (*2*) 0.045% $K_2Cr_2O_7$, 0.035% Na_2SO_3; (*3*) 0.04% $K_2Cr_2O_7$, 0.03% Na_2SO_3; (*4*) 0.035% $K_2Cr_2O_7$. 0.03% Na_2SO_3; (*5*) 0.03% $K_2Cr_2O_7$, 0.02% Na_2SO_3; (b) (*1*) 0.05% $K_2Cr_2O_7$, 0.04% Na_2SO_3; (*2*) 0.035% $K_2Cr_2O_7$, 0.03% Na_2SO_3; (*3*) 0.02% $K_2Cr_2O_7$, 0.02% Na_2SO_3; (*4*) no hardeners. Shear rate 16 s^{-1}; composition temperature (a) 30°C and (b) 40°C.

Na_2SO_3. When the temperature is raised to 40°C, the gelation time gets shorter and viscosity gets loser by about a factor of 1.5, and, therewith, efficient gelation is observed at lower concentrations of hardeners: 0.035% $K_2Cr_2O_7$ and 0.03% Na_2SO_3. Curves *1* and *2* in Fig. 2b have maxima, implying complete gelation of the sample.

Thus, the research on the rheological properties of an aqueous explosive composition established that the shear rate and temperature affect the rheological behavior of the composition until cross-linking has completed. It was shown that the apparent gelation temperature of the polyacrylamide composition studied is 30°C at the following concentration of the hardening agents: 0.045% $K_2Cr_2O_7$ and 0.04% Na_2SO_3.

CONCLUSIONS

The introduction of polyacrylamide as a flocculant in nitrocellulose manufacturing wastewaters makes possible their purification up to the level of drinking water quality.

Another use of polyacrylamide in the process of utilization of nitrocellulose manufacturing wastes is as a thickener for aqueous explosive compositions on the basis of an intermediate product of nitrocellulose manufacturing. The established manufacturing process parameters for the aqueous explosive composition prevent sedimentation of the active filler and stratification of the system.

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