Preparation of a Flocculant Based on Polyamides

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Synopsis

A flocculant based on waste oligomers from the polycaprolactam production was synthesized by alkaline reduction with Ni/Al alloy. Both the reduced oligoamide and the sodium aluminate are precipitated by methanol. An oligomer, absorbed by a mineral carrier, is isolated as final product. The modified oligoamide was characterized by elemental analysis, IR spectra, and was shown to contain hydroxyl groups. The prepared flocculant may be used for the clarification of natural dilute (1%) clay suspensions and wastewaters. It accelerates the precipitation 35 times, giving a compact precipitate, which favors the decanting of the clarified liquid. The optimal concentration of the flocculant is 1.8 g/liter (corresponding to 0.06 g/liter oligomer).

INTRODUCTION

The purification of rivers and wastewaters is one of the major environmental problems to which the research on new flocculants is directed. In this field organic polymers are increasing in importance.

Polymers and copolymers of acrylamide have been used for the purification of coal clay suspensions[1] and of wastewaters from pulp production.[2] High molecular weight flocculants based on glycerol,[3] starch,[4] alkylenediaminoepichlorhydrin, or its salts[5] have been suggested. These flocculants have not been put to practical use, because these are high-costing or difficult to synthesize products which are used in high concentrations.

Modifications of polyacrylamide such as Separan (USA), Acrylax (Czechoslovakia), and PAA in various forms (USSR) are prepared by polymerization of monomers, e.g., acrylamide, or by copolymerization of acrylamide with methacrylamide, followed by treatment of the product with acids and bases.[6]

The preparation by Separan AP-30, considered to be one of the most effective flocculants, necessitates a preliminary purification of the acrylamide which is a slow and difficult process. It is applied in the form of a water solution the preparation of which obviously takes time and requires special equipment. When Separan is used for the isolation of fine clay particles in the production of porcelain, its washing out of the precipitate is quite difficult.

The present paper treats the synthesis and the properties of a flocculant based on polyamide and intended for the clarification of natural dilute clay suspensions and wastewaters.[7] It combines the positive qualities of polymeric and inorganic flocculants. It is highly effective, used in comparatively low concentrations, and gives compact precipitates favoring the decanting of the clarified liquid. The product is highly soluble in water and thus does not contaminate the precipitate. It is added directly to the suspensions and to the wastewaters without preliminary solution.

The modified oligoamide is prepared from waste oligomers from the production of polycaprolactam by reduction with Ni/Al alloy in an alkaline medium (26% sodium hydroxide).

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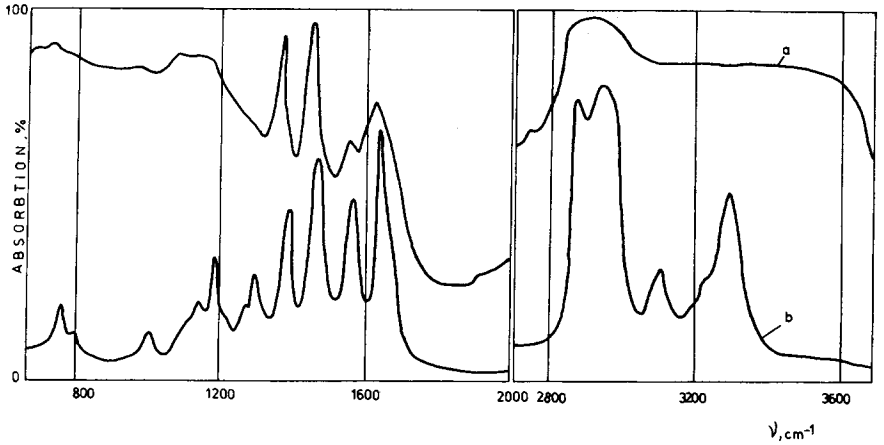


Fig. 1. IR spectra of the oligomers: (a) reduced oligoamide; (b) starting oligoamide.

TABLE I
Elemental Analysis

Elements	Reduced oligoamide		Starting oligoamide
	Calculated, %	Obtained, %	Obtained, %
C	71.4	70.9	64.5
H	13.0	11.8	9.8
N	14.0	13.8	11.3
O	1.6	3.5	14.4

TABLE II
Comparative Data for the Clarification Time of Clay Suspensions by the Reduced Oligoamide and Separan AP-30

No.	Flocculant	Concentration of clay suspension, %	Concentration of the flocculant, g/l.	Time of clarification, min	Type of precipitate
1	None	1	—	222	loose
2	Separan AP-30	1	0.06	30	loose
3	Reduced oligomer	1	0.06	6	compact
4	None	10	—	514	loose
5	Separan AP-30	10	0.06	8	compact
6	Reduced oligomer	10	0.06	16	compact

EXPERIMENTAL

Waste oligomers from polycaprolactam production with an average molecular weight of 1000, or oligoamides with a molecular weight of 800 to 2300, obtained by polymerization of ϵ-caprolactam in the presence of acetic acid at 200°C for 2 hr are used as starting materials in the preparation of the new polymeric flocculant.

In a 250-ml flask 1 g oligoamide is suspended in 50 ml 26% sodium hydroxide, and 10 g of a 50% Ni/Al alloy "Merck" is added to the suspension, the whole mixture being cooled by ice. Then the mixture is heated for 4 hr at 80°C on a water bath. Nickel is removed by centrifuging after the end of the reaction. Sulfuric acid is added to supernatant layer consisting of a polymer suspension

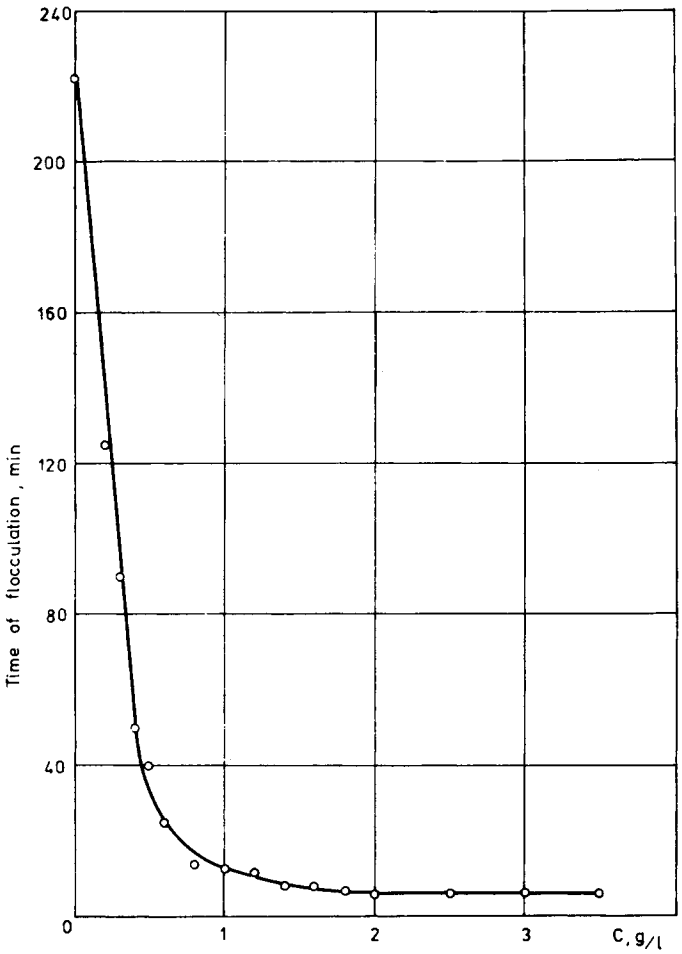


Fig. 2. Relationship between precipitation time of 1% clay suspensions and concentration of the flocculant.

until the polymer is dissolved. After that it is neutralized with 30% sodium hydroxide, and both the reduced product and sodium aluminate are coprecipitate with methanol. The precipitate is filtered and dried at room temperature.

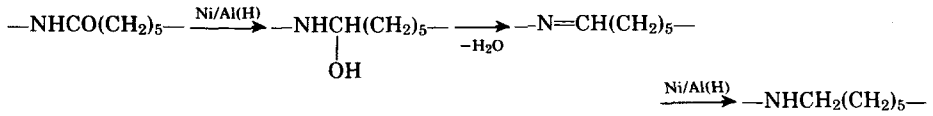
Characteristic for the method is that under the given conditions the final product present is absorbed over a mineral carrier. As a by-product pure nickel sulfate, which may be used for nickel plating, can be obtained from the spent reducing agent after dissolving in sulfuric acid.

The modified oligoamide was characterized by elemental analysis and IR spectra. It was prepared for this purpose without a carrier. The hydroxyl groups were determined by titration with p-BrC_6H_4COCl in a pyridine–toluene solution.[8]

The product was studied for its flocculating action upon clay suspensions. The quantity of the colloidally dissolved substances was measured by the transparency of water samples. This was done visually by comparing the turbidities. The nephelometer of Pulfrih may be used for lower concentrations of the clay suspensions.

RESULTS AND DISCUSSION

The process of reduction of the oligoamide with Ni/Al alloy takes place according to the following scheme:



The isolated pure, reduced oligoamide contains 1.6% hydroxyl groups. Their presence is indicated by the bands at 1000–1100 cm^{-1} and 3300 cm^{-1} in the IR spectrum (Fig. 1). The elemental analysis (Table I) shows an increase of hydrogen content from 9.8% to 11.8% and a sharp decrease in the content of oxygen, which was determined indirectly. The molecular mass is nearly the same as that of the starting product—an indication that the macromolecules do not undergo destruction.

The prepared oligomer was studied as a flocculant for 1% and 10% clay suspensions and compared to the action of Separan AP-30 under the same conditions.

The flocculation time of 1% clay suspensions was plotted against the concentration of the reduced oligoamide, absorbed on the sodium aluminate (Fig. 2) in order to determine the optimum concentration of the flocculant, c (1.8 g/liter or 0.06 g/liter oligomer).

The data for the time of suspension clarification are given in Table II. It is clearly seen that for dilute (1%) clay suspensions the new flocculant possesses high efficacy. It accelerates the precipitation 35 times, giving a compact precipitate, which favors the separation of the clarified liquid. Under the same concentrations the Separan AP-30 precipitates the clay particles five times slower than the flocculant in this paper, and besides, the precipitate is a loose one. Separan AP-30 clarifies more concentrated suspensions quicker than the reduced oligoamide, but the precipitate is not compact and the flocculant is retained in it.

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