

The Effects of Branching and Other Physical Properties of Anionic Polyacrylamides on the Flocculation of Domestic Sewage

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Synopsis

This investigation was undertaken to evaluate the effect of long-chain branching of anionic polyacrylamides on the flocculation of domestic sewage. The polyelectrolytes were polymerized using a redox couple, selectively hydrolyzed, and then characterized by means of light-scattering photometry. Coagulation tests were then employed to evaluate the synthesized polymers. The optimum polymer dose for suspended solids removal was used as the basis for evaluating each anionic polyacrylamide fraction with respect to its ability to flocculate domestic sewage. The results of this investigation indicated that as the weight-average molecular weight increased, the optimum polymer dose decreased. For polymers of similar molecular weights and differing radii of gyration, as the radius of gyration increased, the optimum polymer dose decreased, indicating that the "linear" polymers were more efficient in removing suspended solids than the "branched" polymers.

INTRODUCTION

In recent years, there has been an increased emphasis on the reduction of water-polluting material that enters streams and lakes from all sources, in particular from sewage treatment plants. This emphasis has prompted the search for chemical additives to improve the operation of existing wastewater treatment facilities. As one phase of this search, an in-plant demonstration was conducted in Cleveland which showed that anionic polyacrylamides significantly improved primary clarification in wastewater treatment.¹

Very little information has been published regarding the effect of the various properties of anionic polyacrylamide on its flocculation activity for domestic sewage. The properties which can be expected to vary between commercial sources are average molecular weight, molecular weight distribution, degree of hydrolysis of the amide groups, degree of branching of the polymer structure, and the presence of impurities. Upon examination of the bridging theory of Lamer and coworkers, it is obvious that these variables do have an effect on the flocculation activity of polymers.²⁻⁵ The

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one most notable property of anionic polyacrylamide which has not been studied with respect to flocculation activity is branching. This investigation was conducted primarily to determine the effect of branching on the flocculation performance of anionic polyacrylamides in the primary clarification of domestic sewage.

EXPERIMENTAL

Polymer Production and Characterization

The polymerization technique utilized a water phase system with a persulfate–metabisulfite redox couple. The polymerizations were performed at two temperatures to produce linear (25°C) and branched (78°C) groups of polymers.⁶ The precipitation and stabilization of the subsequent polymers were carried out in the same step by the addition of methanol and filtered compressed air to the reaction vessel.⁷ The stabilized polymers were then dried in a vacuum oven at 28°C before storage.

The polymers produced by the above method had an unknown degree of hydrolysis. For this investigation, the polymer samples were split and the two portions were hydrolyzed to 25% and 35% levels, respectively. The technique to determine the initial and the resultant final degree of hydrolysis was as follows. A known amount of polymer was dissolved in distilled water, acidified with hydrochloric acid to a pH below 3.3, and back titrated to a pH of 7.0. The number of equivalents of base required to bring the polymer solution from a pH of 3.3 to 7.0 equaled the number of equivalents of combined acrylic acid moieties in the sample. As a baseline value, a sample of acrylamide was used to determine a value for the number of equivalents of base used for a sample with no hydrolysis.⁸ Twenty-four hours after base addition and before reprecipitation were allowed in order to achieve the desired degree of hydrolysis.

The polymer characterization was performed using a Brice Phoenix 1000 Å light-scattering photometer. The calibration medium was tungstosilicic acid in a 0.1 molar NaCl solution.⁹ All solutions used in the light-scattering analysis were filtered under moderate pressure through a 0.45-micron filter. All polymers were analyzed at 5461 Å and examined between 25° and 90° at dilutions of either four, five, or six times the original polymer concentration. The varying concentrations of polymers were obtained by direct dilution in the light-scattering cell. For each of the light-scattering runs, the temperature in the sample cell was maintained at $25.0 \pm 0.1^\circ\text{C}$. A computer program which utilized the double extrapolation technique of Zimm was used to reduce the data to arrive at the weight-average molecular weight and radius of gyration.¹⁰ All reported molecular weights in this paper are weight-average molecular weights.

Flocculation Evaluation

Following polymer production and characterization, the optimum polymer dose and the effect of the various polyacrylamides on primary sewage clarification were determined. The optimum polymer dose in this

investigation was defined as the application dosage of the specific polymer which gave the highest refiltration rate. By theory, this occurred when optimum surface coverage was achieved by the polymer.^{2-5,11} Following determination of the optimum polymer dose, coagulation "jar tests" were conducted to define suspended solids removal for that dose.

All the flocculation tests that were conducted in the optimum dose determinations and in the jar tests for evaluation of suspended solids removal were run using 1 liter of sewage at room temperature. The flocculation jar test consisted of a 30-sec rapid mix at 70 rpm and a 15-min slow mix at 10 rpm. During the rapid mix sequence, appropriate cations were first added and then the polymer. Following the end of the slow mix period, the sample was allowed to settle for 10 min.

Before running the refiltration tests for the optimum polymer doses of the various polyacrylamides, an investigation of the minimum cation concentration necessary for adequate bridging was conducted using constant doses of commercially available Dow Purifloc A-23. Calcium concentration was varied, and refiltration rates for each cation level were determined.

The refiltration tests to determine the optimum polymer dosage were completed in the following manner. After the 10-min settling period, 800 ml of the clarified sewage was decanted. The remaining 200 ml was filtered under a vacuum of 14.5 in. Hg. The time required to collect 100 ml was recorded. This process was repeated with varying polymer doses at a constant hardness level until a maximum refiltration rate was ascertained. This rate was associated with the optimum polymer dose.

The jar tests for determining suspended solids reductions for the optimum polymer doses were run separately from the optimum polymer dose determinations due to time and storage limitations. The optimum polymer doses were again applied to raw sewage, and the corresponding suspended solids reductions were determined. Each optimum dose was tested five times so that a reasonable number of experimental values were obtained for statistical analysis.

RESULTS

The polymerization conditions and the characterization results are presented in Table I and Figure 1. Figure 1 gives the relationship between the radius of gyration and the average molecular weight. Although the desired molecular weight variations were achieved, no distinct groups of "linear" and "branched" polymers were found. This result was due to the Tromsdorf effect during the polymerization process as substantiated by the relatively high per cent conversions listed in Table I. Although there were no distinct groupings of "linear" and "branched" polymers, there was sufficient spread in the average molecular weight and the radius of gyration to investigate the effect of branching on the flocculation of domestic sewage.

Figure 2 represents the relationship between the divalent cation level and the refiltration rate parameter for the determination of the minimum divalent cation concentration necessary to achieve satisfactory bridging

TABLE I
Polymerization and Light-Scattering Results^a

| Polymer fraction no. | Temp., °C | Metabisulfite level, g | Persulfate level, g | Conversion, % | Final degree of hydrolysis, % | Weight-average mol. wt. g/mole | Error as % of mol. wt. ^b | Radius of gyration, Å |
|----------------------|-----------|------------------------|---------------------|---------------|-------------------------------|--------------------------------|-------------------------------------|-----------------------|
| 1-25-25 | 25 | 0.0048 | 0.0200 | 34 | 25.1 | 1,514,000 | 18.51 | 1747 |
| 1-25-35 | 25 | 0.0048 | 0.0200 | 34 | 35.0 | 1,192,000 | 22.97 | 1693 |
| 2-25-25 | 25 | 0.0142 | 0.0595 | 75 | 24.8 | 191,000 | 11.25 | 1100 |
| 2-25-35 | 25 | 0.0142 | 0.0595 | 75 | 35.0 | 151,500 | 13.41 | 1164 |
| 3-25-25 | 25 | 0.0710 | 0.2960 | 35 | 25.2 | 605,500 | 14.92 | 3993 |
| 3-25-35 | 25 | 0.0710 | 0.2960 | 35 | 35.2 | 340,400 | 27.13 | 2825 |
| 4-25-25 | 25 | 0.0024 | 0.0100 | 64 | 25.0 | 8,224,000 | 8.94 | 6055 |
| 4-25-35 | 25 | 0.0024 | 0.0100 | 64 | 34.8 | 18,205,000 | 4.16 | 8977 |
| 1-78-25 | 78 | 0.0048 | 0.0200 | 39 | 25.0 | 325,000 | 8.89 | 1709 |
| 1-78-35 | 78 | 0.0048 | 0.0200 | 39 | 35.0 | 306,400 | 8.81 | 1571 |
| 2-78-25 | 78 | 0.0142 | 0.0595 | 70 | 24.9 | 171,600 | 14.51 | 1329 |
| 2-78-35 | 78 | 0.0142 | 0.0595 | 70 | 34.7 | 189,500 | 13.97 | 1431 |
| 4-78-25 | 78 | 0.0010 | 0.0041 | 18 | 25.1 | 836,700 | 19.72 | 4217 |
| 4-78-35 | 78 | 0.0010 | 0.0041 | 18 | 33.9 | 765,000 | 15.36 | 3896 |
| 4a-78-25 | 78 | 0.0024 | 0.0100 | 21 | 24.9 | 3,470,000 | 15.45 | 2099 |
| 4a-78-35 | 78 | 0.0024 | 0.0100 | 21 | 35.0 | 3,316,000 | 16.29 | 2027 |

^a The following conditions were constant for all the reactions: 2.5 liters of deionized water passed through a 0.45-micron filter; 250 g acrylamide; Reaction mixture was purged for 1 hr before catalyst addition and then continued for course of reaction.

^b Possible error in the intercept of the Zimm plot by double extrapolation.

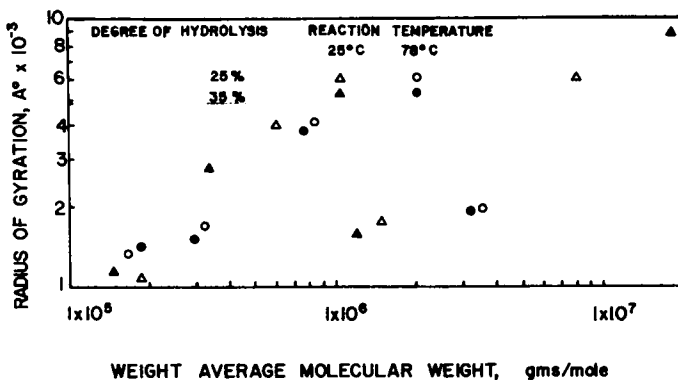


Fig. 1. Relationship between average molecular weight and radius of gyration.

of the anionic polyacrylamides to the suspended solids. This part of the investigation utilized Dow Purifloc A-23 as the polymer to test the divalent cation effect. The minimum acceptable divalent cation level was found to be approximately 110 mg/l. as calcium.

Table II lists the results of the refiltration tests for the determination of the optimum polymer doses. Figure 3 is included to illustrate the data taken for each polymer fraction and the method by which the optimum

TABLE II
Optimum Polymer Doses for the Polyacrylamides

| Polymer fraction no. | Weight-average mol. wt, (g/molé) $\times 10^{-6}$ | Radius of gyration, Å | Optimum polymer dose, mg/l |
|----------------------|---|-----------------------|----------------------------|
| 1-25-25 | 1.514 | 1747 | 1.2 |
| 1-25-35 | 1.192 | 1693 | 1.2 |
| 2-25-25 | 0.191 | 1100 | 2.3 |
| 2-25-35 | 0.151 | 1164 | 2.5 |
| 3-25-25 | 0.605 | 3993 | 1.5 |
| 3-25-35 | 0.340 | 2825 | 1.6 |
| 4-25-25 | 8.224 | 6055 | 0.3 |
| 4-25-35 | 18.221 | 8977 | 0.2 |
| 1-78-25 | 0.325 | 1709 | 1.9 |
| 1-78-35 | 0.306 | 1571 | 1.9 |
| 2-78-25 | 0.171 | 1329 | 2.4 |
| 2-78-35 | 0.189 | 1431 | 2.4 |
| 4-78-25 | 0.836 | 4217 | 1.4 |
| 4-78-35 | 0.765 | 3896 | 1.6 |
| 4a-78-25 | 3.470 | 2009 | 1.0 |
| 4a-78-35 | 3.320 | 2027 | 0.9 |

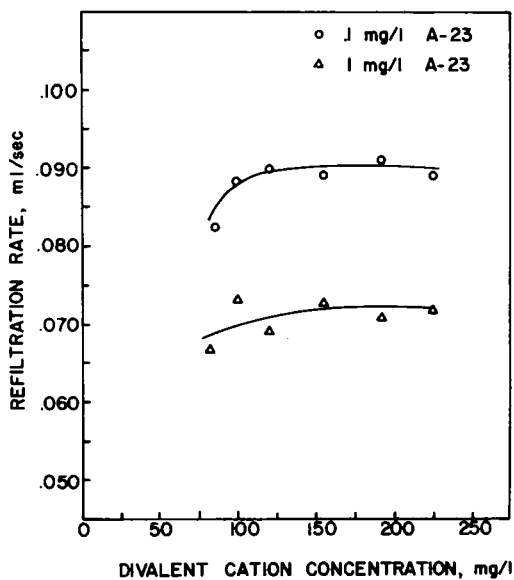


Fig. 2. Refiltration rate as a function of divalent cation concentration in the determination of minimum cation level for effective bridging using Dow A-23 polymer.

dose was determined by finding the maximum refiltration rate. Figure 4 is the relationship between the optimum polymer dose and the average molecular weight of the various polymer fractions. The one notable relationship from this figure is the high degree of correlation between the optimum polymer dose and the average molecular weight.

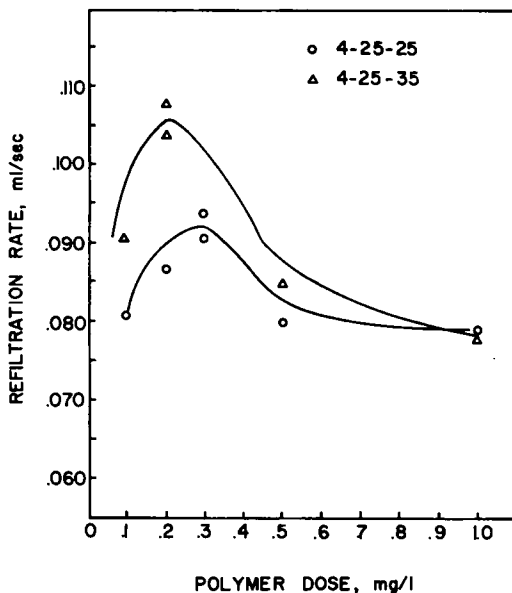


Fig. 3. Typical determination of optimum dose of selected synthesized polymer fractions.

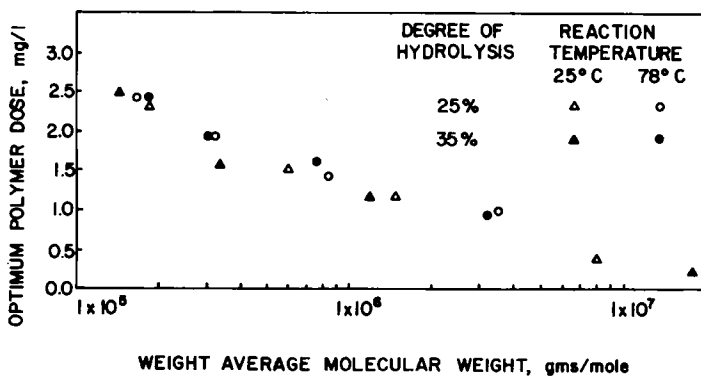


Fig. 4. Relationship between average molecular weight and optimum polymer dose.

STATISTICAL CONSIDERATIONS

The statistical significance of the experimental results for the various polyacrylamide fractions was determined by use of several techniques. Table II and Figure 4 relate the optimum polymer doses for the various polyacrylamide fractions synthesized in this investigation. The only trend that can be readily gleaned from these data is that as the average molecular weight decreases, the optimum polymer dose increases. In order to determine the effect of branching, a statistical test commonly called analysis of variance (anova) was employed to allow determination as to whether the effect of radius of gyration given the effect of the average molecular weight on the optimum polymer dose was statistically significant.

TABLE III
Anova Analysis of Optimum Polymer Doses in Sequential Analysis
at Lower Solids Level

| Source | Degrees of freedom | Sum of squares | Mean squares | F-Value |
|--|--------------------|----------------|--------------|-----------|
| Regression due to weight-average molecular weight and radius of gyration | 2 | 7.2195 | 3.6098 | 165.580** |
| Regression due to weight-average molecular weight | 1 | 7.1598 | 7.1598 | 328.430** |
| Regression due to radius of gyration given the effect of weight-average molecular weight | 1 | 0.0597 | 0.0597 | 2.738*** |
| Residual | 14 | 0.3050 | 0.0218 | |
| Total | 16 | | | |

| F-Tabulated Values Necessary for Significance | | |
|---|---------------------------|---------|
| Degrees of freedom | α Protection level | F-Value |
| (2, 14) | 0.05* | 3.74 |
| (1, 14) | 0.01** | 6.51 |
| | 0.05* | 4.60 |
| | 0.01** | 8.86 |
| | 0.15*** | 2.43 |

The results of the anova test for experimental work in which sewage with a relatively low level of suspended solids was employed are given in Table III. In this anova the optimum polymer dose was correlated with the logs of the weight-average molecular weight and radius of gyration. The reason for this transformation is that the anova variables must be linear with respect to each other by definition for the anova to be statistically valid.

The regression due to the average molecular weight yielded an F -statistic of 328.43 and thus indicated a highly significant correlation at the 99% confidence level. This result means that the effect of the average molecular weight is very important in determining the optimum dose parameter. The regression due to both variables gave an F -statistic of 165.58, again highly significant, but less than the case where only the average molecular weight was correlated. The regression due to the radius of gyration alone given the effect of the average molecular weight was significant but at a lower, 85% confidence level. Essentially this result means that in this anova, the radius of gyration of the various polyacrylamides does have a statistical bearing on the total regression model. The model in simplified terms implies that a better than 99% probability exists that the molecular weight is important in the regression. With respect to radius of gyration, the model implies that an 85% probability exists that the radius of gyration is important in the regression. This lower significance level is the reason why the regression due to both variables was less than that due only to the weight-average molecular weight.

TABLE IV
Experimental Results for Suspended Solids Removal Using
Synthesized Polyacrylamides

| Polymer fraction no. | Increase in suspended solids removal using previously determined optimum dose | |
|----------------------|--|--------------------|
| | Low-solids system | High-solids system |
| 1-25-25 | 21.09% | 26.7% |
| 1-25-35 | 24.28 | 21.9 |
| 2-25-25 | 8.11 | — |
| 2-25-35 | 8.74 | — |
| 3-25-25 | 13.14 | — |
| 3-25-35 | 10.92 | 37.6 |
| 4-25-25 | 29.74 | — |
| 4-25-35 | 24.60 | — |
| 1-78-25 | 8.89 | — |
| 1-78-35 | 8.94 | — |
| 2-78-25 | 8.17 | — |
| 2-78-35 | 5.82 | — |
| 4-78-25 | 16.12 | 37.6 |
| 4-78-35 | 20.87 | 37.5 |
| 4a-78-25 | 26.34 | 24.1 |
| 4a-78-35 | 24.17 | 22.7 |

In summarizing this portion of the analysis, the effect of the average molecular weight was found to be very important in determining optimum polymer dose. The optimum polymer dose increases as the average molecular weight decreases. This trend is easily recognized in Figure 4. The effect of the radius of gyration was also found to be important in determining the optimum polymer dose. For similar molecular weight and different radius of gyration, the larger the radius of gyration, the lower the optimum polymer dose. For example, a polymer with a molecular weight of 325,000 g/mole and a radius of gyration of 1709 Å had an optimum dose of 1.9 mg/l., while a polymer with a molecular weight of 340,000 g/mole and a radius of gyration of 2825 Å had an optimum dose of 1.6 mg/l. The second conclusion, therefore, implies that the extent of branching of the polymer chain has a significant effect on the optimum polymer dose.

After determining the optimum polymer doses for the various polymer fractions, an investigation of the suspended solids removal when using these optimum polymer doses was undertaken in order to determine the efficiency of flocculation of domestic sewage and to ascertain the effect of varying the degree of polymer hydrolysis from 25% to 35%. Improvement in suspended solids removal due to polymer usage is indicated by the data given in Table IV.

In the anovas designed to analyze for significant differences in per cent removals of suspended solids, Tables V, VI, and VII, the *F*-statistic in both the high- and low-solids systems was highly significant. This result eliminated the possibility that the optimum polymer doses were all equally

TABLE V
Anova Analysis of Per Cent Solids Removals Employing the Optimum Polymer Doses and Duncan's Multiple Range Tests at Lower Solids Level

| Source | Degrees of freedom | Sum of squares | Mean squares | F-Value |
|-----------|--------------------|----------------|--------------|---------|
| Treatment | 15 | 4839.0 | 321.2 | 21.6** |
| Error | 64 | 959.5 | 14.8 | |
| Total | 89 | 5798.5 | | |

| F-Tabulated Value Necessary for Significance | | |
|--|---------------------------|---------|
| Degrees of freedom | α Protection level | F-Value |
| (15,64) | 0.05* | 1.84 |
| | 0.01** | 2.35 |

| Duncan's Multiple Range Test at One Per Cent (Polymer and Removal) | | | | | | | | |
|--|----------|---------|---------|----------|---------|---------|---------|---------|
| 4-25-25 | 4A-78-25 | 4-25-35 | 1-25-35 | 4A-78-35 | 1-25-25 | 4-78-35 | 4-78-25 | 3-25-25 |
| 29.74 | 26.34 | 24.60 | 24.28 | 24.17 | 12.09 | 20.87 | 16.12 | 13.14 |

| | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|-----|
| | | | | | | | (A) |
| 3-25-35 | 1-78-35 | 1-78-25 | 2-25-35 | 1-78-25 | 2-25-25 | 2-78-25 | |
| 10.92 | 8.94 | 8.89 | 8.74 | 8.17 | 8.11 | 5.82 | |

(A)

efficient in removing solids. It must be remembered that the term "optimum polymer dose" only implies the highest solids removal for that individual polymer. The differences in the suspended solids removals for the various optimum polymer dosages might be attributable to one of several factors. First, the different polymer fractions may by nature of their physical properties have varying residual amounts of polymer left in solution and not used in bridging. Second, the molecular weight distributions of the polymers may have an effect on the bridging. Finally, the size or radius of gyration of the polymer molecule in solution may greatly affect the shear strength of the floc particles.

Duncan's Multiple Range Test was also conducted and is presented to compare the treatment results. The purpose of Duncan's test was to examine the removals obtained for each polymer fraction to see if these removals differed to a statistically significant degree from each other. Those polymer fractions commonly underlined were not significantly different from each other and can be assumed to yield the same removal. With regard to the degrees of hydrolysis, no distinction was discerned from Duncan's test as noted in Tables V through VII. From the standpoint of solids removal, neither degree of hydrolysis consistently showed any better effect than the other on the removals obtained. Therefore, the

TABLE VI
Comparison of Selected Polymer Fractions at the Lower Solids Level Using
Optimum Polymer Doses and Duncan's Multiple Range Tests

| Source | Degrees of freedom | Sum of squares | Mean squares | <i>F</i> -Value |
|-----------|--------------------|----------------|--------------|-----------------|
| Treatment | 6 | 594.2 | 99.0 | 6.07** |
| Error | 28 | 456.2 | 16.3 | |
| Total | 34 | 1050.4 | | |

| <i>F</i> -Tabulated Value for Necessary Significance | | |
|--|---------------------------|-----------------|
| Degrees of freedom | α Protection level | <i>F</i> -Value |
| (6,28) | 0.05* | 2.45 |
| | 0.01** | 3.53 |

| Duncan's Multiple Range Test at Five Per Cent (Polymer and Removal) | | | | | | |
|---|---------|---------|---------|----------|---------|----------|
| 3-25-25 | 4-78-25 | 4-78-35 | 1-25-25 | 4A-78-35 | 1-25-35 | 4A-78-25 |
| 13.1 | 18.2 | 20.9 | 21.1 | 24.2 | 24.3 | 26.3 |

TABLE VII
Comparison of Selected Polymer Fractions at the Higher Solids Level Using
Scaled Optimum Polymer Doses and Duncan's Multiple Range Tests

| Source | Degree of freedom | Sum of squares | Mean squares | <i>F</i> -Value |
|-----------|-------------------|----------------|--------------|-----------------|
| Treatment | 6 | 1667.4 | 277.9 | 33.5** |
| Error | 28 | 232.8 | 8.3 | |
| Total | 34 | 1900.4 | | |

| <i>F</i> -Tabulated Value for Necessary Significance | | |
|--|---------------------------|-----------------|
| Degrees of freedom | α Protection level | <i>F</i> -Value |
| (6,28) | 0.05* | 2.45 |
| | 0.01** | 3.53 |

| Duncan's Multiple Range Test at Five Per Cent (Polymer and Removal) | | | | | | |
|---|----------|----------|---------|---------|---------|---------|
| 1-25-35 | 4A-78-35 | 4A-78-25 | 1-25-25 | 4-78-35 | 4-78-25 | 3-25-25 |
| 21.9 | 22.7 | 24.1 | 26.7 | 37.5 | 37.6 | 37.6 |

conclusion was drawn that there was no appreciable difference between 25% and 35% hydrolysis of the polyacrylamides on the suspended solids removal from domestic sewage.

At the conclusion of the previously described jar tests, it was decided to investigate several selected polymers using sewage with a higher solids level to test the effect of large radius of gyration differences and relatively small weight-average molecular weight differences. Seven polymers were chosen. Three "linear" polymers, 4-78-35, 4-78-25, and 3-25-25, and four "branched" polymers, 1-25-25, 4A-78-25, 4A-78-35, and 1-25-35, were investigated on the higher solids level. (The "linear" polymers listed

above include polymers produced at 25° and 78°C, and the "branched" polymers also include those polymerized at 25° and 78°C. The Tromsdorf effect apparently partially masked the effect of temperature on the polymer chain formation.) Tables VI and VII are the comparisons of the selected polymers at the lower, previously used solids level and the higher solids level, respectively. The results at the lower solids level test revealed virtually no trend with respect to the size and shape differences. But the results at the higher solids level demonstrated the fact that with relatively small differences in the weight-average molecular weights, the more linear polymers yielded a higher solids removal. For example, in the flocculation tests, a polymer of 836,000 g/mole and 4217 Å removed an additional 37% of the suspended solids, while a polymer of 3,316,000 g/mole and 2027 Å removed only an additional 23% of the suspended solids. Thus, the conclusion may be drawn that long-chain branching in anionic polyacrylamides decreased the solids removal during flocculation.

In the Cleveland Easterly Treatment Plant study using Dow Purifloc A-23, it was reported that the addition of polymer increased the suspended solids removal in the primary clarifier by 39% when treating raw sewage with a suspended solids content of about 160 mg/l. The maximum increase in removal obtained in this investigation was 37% for raw sewage with a suspended solids level of 152 mg/l. Therefore, the polymers synthesized for this investigation were satisfactory with respect to suspended solids removal, and results were comparable to those obtained at Cleveland.

CONCLUSIONS

The investigation of the effect of branching and other properties of anionic polyacrylamides on the flocculation of domestic sewage led to the following conclusions:

1. As the weight-average molecular weight increased, the optimum polymer dose decreased.
2. For polymers of similar molecular weight and differing radius of gyration, as the radius of gyration increased, the optimum polymer dose decreased.
3. There was no statistically significant difference in the degree of treatment between 25% and 35% hydrolyzed polymer fractions.
4. For polymers of similar molecular weight and differing radius of gyration, the "linear" polymers were more efficient in removing suspended solids. Therefore, long-chain branching in anionic polyacrylamides decreased the flocculation efficiency in domestic sewage.

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