

# APPLICATIONS OF FLOCCULANTS IN THE CARBONATATION REFINING PROCESS

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## Abstract

The use of cationic flocculants in the carbonatation refining process has been investigated. A large range of flocculants has been screened under optimum conditions. Some of these flocculants have been found to produce a positive influence on impurity removal.

## Introduction

It has previously been demonstrated that flocculants have a beneficial effect on the phosphatation refining process<sup>1,2,3</sup>. Therefore it was decided to investigate their activity within the carbonatation refining process. Bennett<sup>4</sup> carried out similar investigations and concluded that only little success could be expected from the addition of flocculants as they were highly pH sensitive. It is believed, however, that many flocculants may still retain their activity during carbonatation if introduced only at specific stages of the process. Furthermore, there are now several flocculants available which are less pH and temperature sensitive.

Although the carbonatation process is highly efficient, it still has to be followed by a decolorisation plant even when VHP raws are refined. The efficiency is usually stretched to the limit when the sugar impurities reach particularly high levels. In these conditions an increase in addition of reagents and/or retention time cannot always compensate for deterioration in raw sugar quality and produce the high purity levels experienced when a VHP raw is refined. Use of auxiliary chemicals may therefore become necessary.

This paper describes the use of various flocculants within the carbonatation process and their influence on impurities under given conditions.

## Experimental

All experimental work was performed using the SMRI laboratory carbonatation and filtration units which have been previously described<sup>5,6</sup>.

### (a) Raw Materials

A composite sample of raw sugar from the terminal and a composite sample of rock lime from Hulett's Refinery were used in all experiments. The analytical data for these samples appear in the appendix.

### (b) Reaction Conditions

Conditions selected were:-

|                         |  |
|-------------------------|--|
| Reaction pH             | 8,5 (at 80°C)  |
| Reaction temperature    | 80°C   |
| Reaction time           | 60 min.  |
| Brix of reaction liquor | 60°  |
| Gas mixture             | 12% CO <sub>2</sub> in air                           |
| Lime                    | 1% CaO on solids<br>(Lime suspension aged for 4 hrs) |

Preliminary experiments indicated that the optimum time for flocculant addition lay between the 30th and 45th minute of the reaction. The 30th minute was thus chosen as the standard addition point for subsequent work. Flocculants were applied as 10% solutions in distilled water.

### (c) Analytical Control

All analyses were performed by SMRI analytical staff utilizing standard SMRI analytical procedures. The following parameters were monitored: colour, starch, conductivity ash, gums, turbidity and filterability. Turbidity was determined from the absorbance (measured on a Zeiss PM 4 spectrophotometer) at 720 nm using a 1 cm cell. Filterability<sup>8</sup> is expressed by

$$f_c = \frac{1,05}{m^m}$$

where "m" is the slope of the graph of reciprocal filtration rate versus cumulative filtrate volume.

### (d) Flocculants

Flocculants utilised were commercially available cationic polymers:

#### (i) Types of Flocculants

- |  |   |
|--|---|
| I Floccotan  | A locally manufactured polymerized wattle extract.  |
| FX   | Standard liquid flocculant molecular wt approx. 40 000.   |
| F  | Dehydrated powder from FX.  |
| A, B, C, D, E  | A specially prepared range of flocculants with increasing molecular weights from approx. 45 000 to approx. 75 000.                                      |
| II Superfloc flocculants   | Manufactured and supplied by S.A. Cyanamid.   |
| Superfloc C513, C515   | Very low in molecular wt.   |
| Superfloc C585, C587, C589   | Recommended for colour removal. Low molecular wt.   |
| Superfloc C572, C577   | Recommended for colour and turbidity removal. Medium molecular wt.  |
| Superfloc C573, C581   | Recommended for turbidity removal. Medium molecular wt.   |
| III Talofloc surfactant (di-octadecyldimethyl ammonium chloride monomer) | Manufactured by Tate and Lyle. Recommended for colour removal in the phosphatation refining process.  |
| IV Bosefloc C45  | A cationic powdered flocculant manufactured by Hoechst. Molecular wt. 1,2 x 10 <sup>6</sup> . Recommended for turbidity removal in water clarification. |
| (ii) Screening   | All these flocculants were tested under the above steady state conditions using various dosage levels. Flocculants                                      |

were added at 25, 50, 75 and 100 ppm. The most efficient impurity removal is achieved between 25 and 50 ppm while with greater doses commensurate improvement in clarification is not obtained. Thus 50 ppm was chosen as a standard for comparison. As is evident from Table 1, all the flocculants had a positive influence on at least one of the measured parameters. Floccotan D, Superfloc C515, C572, C577 and C585 appeared to have the most promising positive influence on residual impurity removal and were used in subsequent work.

#### (e) Reaction Procedure

The carbonation process is initiated by the controlled addition of lime to the 60,0° Bx reaction liquor in order to raise the pH from its natural value of around pH 6,3 to the reaction pH of 8,5. The addition rate is such that the reaction pH is attained after 5,0 min. This procedure allows for the nucleation of calcium carbonate seed crystals and ensures the production of sufficient crystals for the whole reaction. During the remainder of the reaction time these crystals are grown under the steady state conditions listed above. The gas flow through the reaction vessel averaged 850 ml/min of the 12% CO<sub>2</sub> in air mixture. The steady state pH of 8,5 at 80°C is maintained by automatic additions of lime until the prescribed amount of 150 ml has been added. After 30 min reaction time the required amount of flocculant is added to the liquor. Evaporation from the reaction surface necessitates frequent adjustment of the brix of the reaction liquor which is maintained at 60,0 by frequent measurement and addition of appropriate amounts of distilled water at approximately 80°C. At the completion of the run, the liquor pH is lowered to 8,0, an amount of 500 ml is withdrawn and the filterability measured. The filtrate collected is immediately shock cooled to 10°C to forestall colour formation at alkaline pH during storage prior to the analysis for residual impurities.

### Results

#### (a) Colour

The additional colour removal achieved with economical dosages of flocculants was disappointing. Using 50 ppm flocculant, additional colour removal of between 10 and 15% was achieved as shown in Fig. 1, whereas at a dose of 150 ppm of the same flocculant under similar conditions the removal increased to 25%.

It was noticed that on changing the point of addition from the 30th to the 45th minute, the same amount of flocculant (50 ppm) removed an equivalent amount of colour as a dose of 150 ppm at the 30th minute. The addition of flocculant immediately prior to filtration had the effect of slightly improving colour removal over the above results. All other impurities as well as filterability were unchanged by flocculant addition at this late stage only Floccotan D decreased the filterability.

During these experiments it was found that the storage of 60° brix filtrates longer than a week at temperatures above 10°C caused a 20% increase in colour as measured at 420 nm. For this reason, filtrates were always shock cooled after collection and analysed as soon as possible in order to reduce the possibility of colour generation.

#### (b) Starch

Starch represents a major impurity component in a raw sugar and thus its removal is of considerable importance <sup>6,7,9,10</sup>. A well run carbonation process removes between 40 and 45% starch. It can be seen from Fig. 2 that the use of 50 ppm flocculant will result in the removal of between 60 and 70% of the total starch. In fact, Superfloc C577 gave a

filtrate containing 35 ppm starch which is comparable to a refined 60° brix solution.

#### (c) Gums

As shown in the Fig. 3, gums are most affected by the application of flocculants. In particular, the use of Superfloc C585 and C577 in carbonation resulted in the removal of 50% of the original gums.

#### (d) Turbidity

Unlike the phosphatation-flotation process which achieves a 100% turbidity removal, carbonation has relatively little effect on turbidity. As illustrated in Fig. 4, the greatest drop in turbidity was achieved with Superfloc C577 which decreased turbidity nearly to the level of a refined sugar solution.

#### (e) Ash

Ash levels (Fig.5) remained unaffected by the application of flocculants except in the case of Superfloc C515 which repeatedly lowered the ash level below the previously determined equilibrium value of 0,10, obtained when Analar Ca (OH)<sub>2</sub> is used.

#### (f) Filterability

All flocculants used at the dosage of 50 ppm decreased to a greater or lesser extent the filterability as compared to a carbonation run without flocculants. As can be seen from Fig. 6, Superfloc C572 and C577 produced the smallest decrease in filterability. The importance of maximising refinery filterability was the underlying reason for choosing the 30th minute as the flocculant addition point since it was noted that flocculant addition in the 45th minute produced markedly inferior filterabilities.

Influence of flocculants when added after completion of the reaction was discussed under "colour removal".

### Discussion

The results indicate that the use of flocculants has a variable influence on the process which depends on the nature of the flocculant and the dosage time. For example, an optimum removal of colour requires the flocculant to be added after saturation. Colour removal involves an instantaneous destabilization of anionic colour bodies and is most effectively achieved prior to filtration, at which point little further colour can be produced by heating under reaction conditions. Although the optimum overall impurity removal was achieved with a flocculant such as Superfloc C577, it was shown that the otherwise ineffective flocculant, Superfloc C515, lowered the ash value which was unaffected by the other flocculants. An unexpected result was the ability of these flocculants to remove substantial amounts of high molecular weight impurities such as gums and starch. A considerable removal of suspended matter (as measured by turbidity) was also achieved. Despite the presence of flocculant and a larger amount of destabilized impurity in the filter cake, filterability was not noticeably influenced.

It was observed that immediately after addition of flocculant, an increase in the speed of reaction occurred. A few runs were performed to investigate these phenomena (Fig. 7). In all these runs steady state conditions were employed and the only parameter studied was the reaction time (at constant pH) required to react the 1% CaO on solids employed (Fig. 8). Flocculant Superfloc C577 was added in all cases to the melt. The addition of 100 ppm flocculant resulted in serious foaming (Fig. 9). The foaming indicates that these flocculants possess some surfactant properties<sup>12</sup>, in particular, they appear to stabilize the air/CO<sub>2</sub> bubbles and thus produce a foaming reaction<sup>13, 14</sup>. This stabilization of reaction gas bubbles is assumed to increase the gas-liquid contact time and thus enhance gassing efficiency

resulting in a faster reaction. The results indicated that additions of up to 75 ppm flocculant would normally produce no foaming problems while additions above 125 ppm would cause difficulties and additions exceeding 250 ppm would cause excessive foaming which would be impossible to handle. Since it is essential to consider the economic costs of flocculant addition, the use of 125 or 250 ppm would, in any case, be ruled out as uneconomic.

As mentioned previously, the use of flocculants should only be considered at times when impurity levels are excessively high. From this point of view, Table 2 shows prices for the 5 chosen flocculants if they were to be employed at 50 ppm in a 26 or 80 t/h raw sugar refinery. The former would be representative of a back-end refinery running approximately 200 days per year, whereas the latter represents Hulett's central refinery running ap-

proximately 260 days per year. When it becomes necessary to handle a sugar of high impurity, eg. high starch, the justification of either 4,5 cents or 9,3 cents per ton of sugar could be considered.

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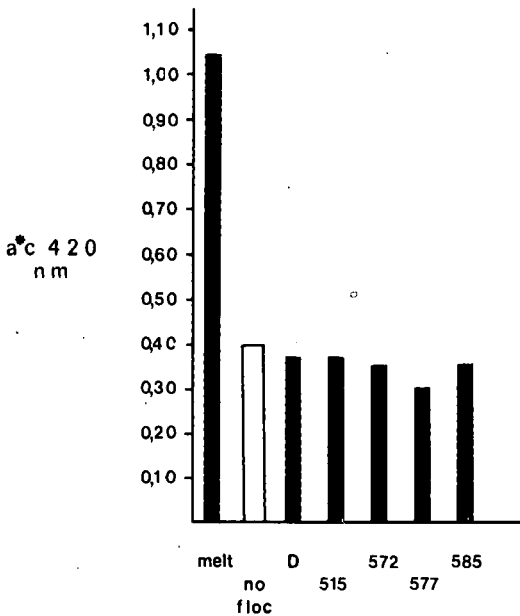


Figure 1: INFLUENCE OF FLOCCULANT (50ppm) ON COLOUR

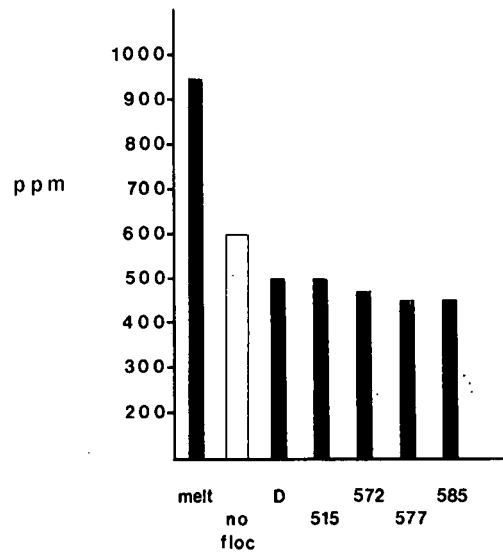


Figure 3: INFLUENCE OF FLOCCULANT (50ppm) ON GUMS

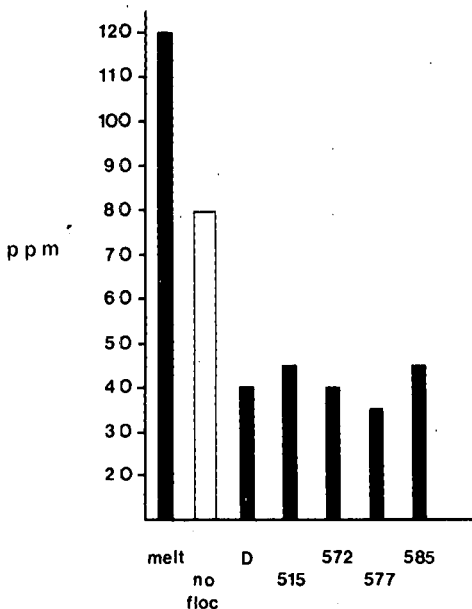


Figure 2: INFLUENCE OF FLOCCULANT (50ppm) ON STARCH

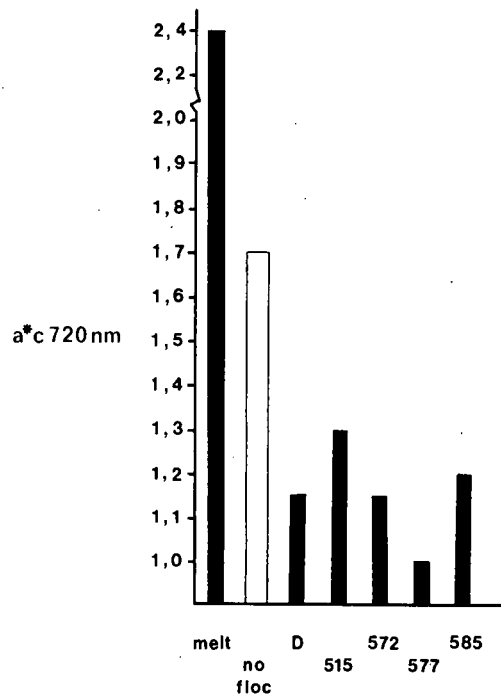


Figure 4: INFLUENCE OF FLOCCULANT (50ppm) ON TURBIDITY

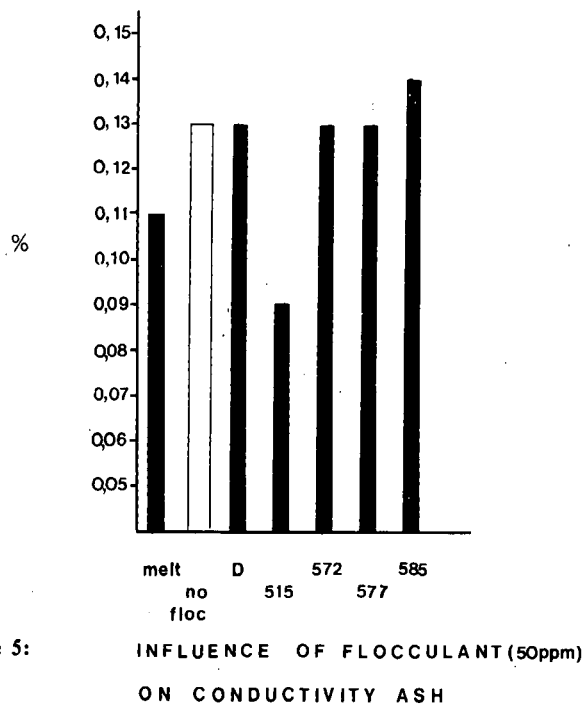


Figure 5:

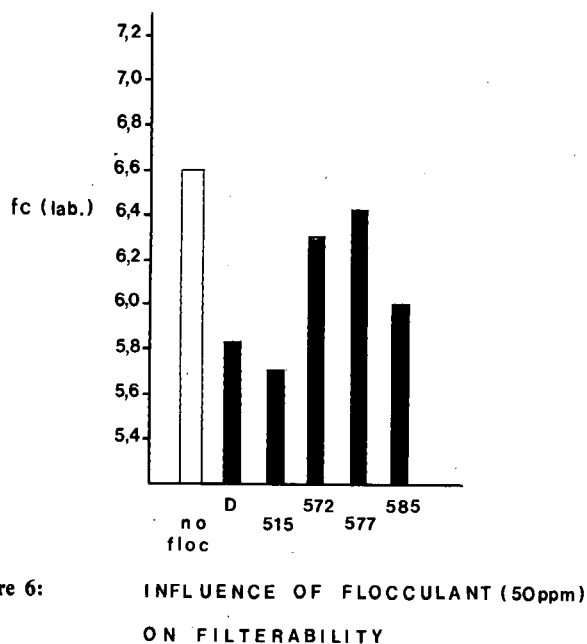


Figure 6:

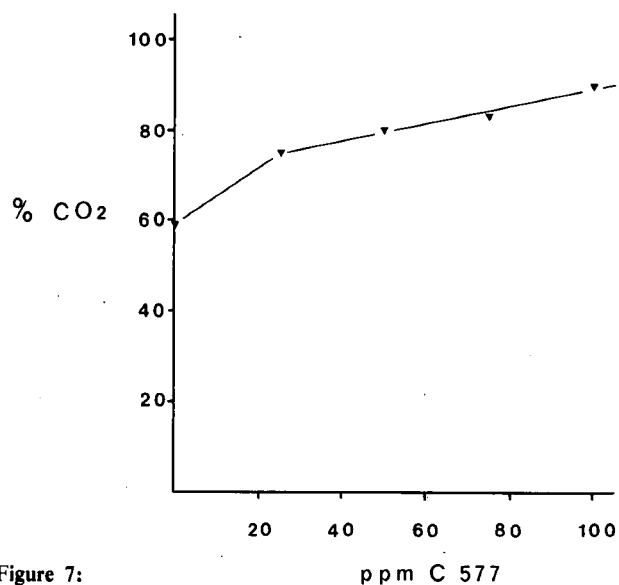


Figure 7:

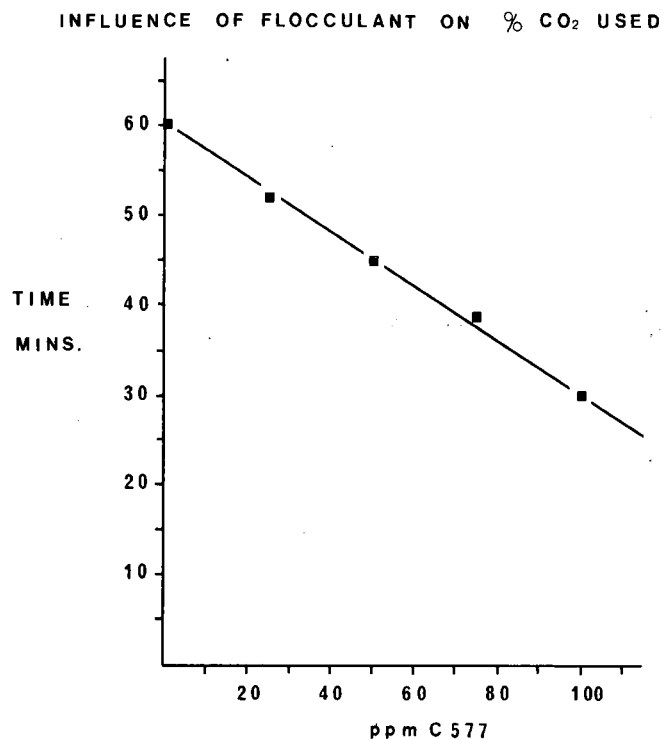


Figure 8:

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**Appendix**

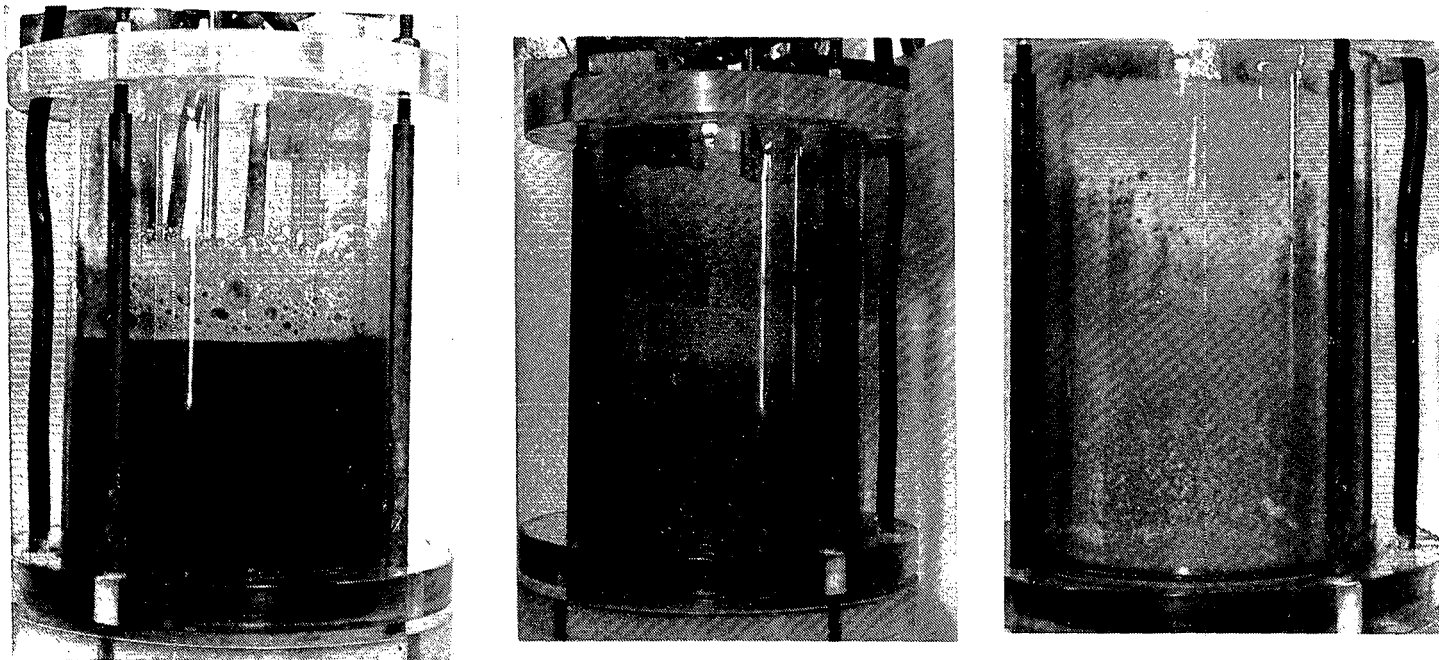
Analytical data on raw sugar used in this study

|                    |   |       |
|--------------------|---|-------|
| Pol °S             | = | 99,54 |
| Moisture %         | = | 0,10  |
| Colour a*c 560 nm  | = | 0,19  |
| Colour a*c 420 nm  | = | 0,88  |
| Conductivity Ash % | = | 0,08  |

|            |   |     |
|------------|---|-----|
| Starch ppm | = | 95  |
| Gums ppm   | = | 650 |

Analytical data on rock lime used in this study

|  |   |      |
|--|---|------|
| CaO %  | = | 91,5 |
| MgO %  | = | 1,0  |
| (Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> ) % | = | 1,1  |



A

B

C

Figure 9:

**INFLUENCE OF FLOCCULANT ON GAS DISTRIBUTION**

A= NO FLOCCULANT

B= 50ppm C 577

C= 250 ppm C577

**TABLE 1**

General behaviour of flocculants on carbonatation

| FLOCCULANT      | COLOUR | STARCH | GUMS | TURBIDITY | CONDASH | FILTERABILITY |
|-----------------|--------|--------|------|-----------|---------|---------------|
| FLOCCOTAN F     | C      | C      | C    | C         | C       | D             |
| " FX            | R      | R      | R    | C         | C       | D             |
| " A             | R      | R      | R    | C         | C       | D             |
| " B             | R      | R      | R    | C         | C       | D             |
| " C             | R      | R      | R    | C         | C       | D             |
| " D             | R      | SR     | SR   | R         | C       | D             |
| " E             | C      | R      | R    | R         | C       | D             |
| SUPERFLOC C 513 | C      | C      | C    | C         | C       | C             |
| " C 515         | C      | C      | C    | C         | B       | D             |
| " C 572         | SR     | R      | R    | SR        | C       | D             |
| " C 573         | R      | R      | R    | R         | C       | D             |
| " C 577         | SR     | SR     | SR   | SR        | C       | C             |
| " C 581         | R      | R      | R    | SR        | C       | D             |
| " C 585         | SR     | SR     | SR   | SR        | C       | D             |
| " C 587         | R      | R      | R    | C         | C       | D             |
| " C 589         | R      | R      | R    | C         | C       | D             |
| TALOFLOC        | C      | C      | R    | R         | C       | D             |
| BOZEFLOC C 45   | C      | R      | R    | R         | C       | D             |

**TABLE 2**

Flocculant costs on refinery scale.

| FLOCCULANT              | R/ kg | 50 ppm /t<br>R | 26t/ 200 days<br>R | 80t/ 260 days<br>R |
|-------------------------|-------|----------------|--------------------|--------------------|
| SUPERFLOC C 515         | 0,50  | 0,025          | 3.120,-            | 14.040,-           |
| SUPERFLOC C 572 / C 577 | 1,26  | 0,063          | 7.861,-            | 35.380,-           |
| SUPERFLOC C 585         | 0,90  | 0,045          | 5.616,-            | 25.272,-           |
| FLOCCOTAN D             | 0,27  | 0,0135         | 1.685,-            | 7.582,-            |