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CLARIFICATION OF WHITE WATER BY
FROTH FLOTATION

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This invention relates to the treatment of waste waters produced in the manufacture of pulp and paper and more particularly to the froth flotation of these waste waters.

In general, the following steps are common to all pulp and paper manufacture. The material whether wood, rags, cotton, cornstalks or any other source of cellulose fibers are broken down into small pieces by chipping, beating, grinding or some equivalent physical treatment. These pieces are then usually given one or more washing steps to remove solid materials, dirt and the like which have no place in the succeeding process steps. Except in the case of news print, these pieces are then passed to some form of cooker or digester in which substantially all the material except the cellulose fibers are converted into a water-soluble condition. After this digesting or cooking step the fibers are given an additional washing step to remove the water soluble products liberated by the cooking. In many cases this is followed up by a bleaching procedure which is again followed by washing. Washed and/or bleached pulp is then fed to a beater engine or some equivalent machine in which the cellulose fibers are subjected to mechanical treatment in the presence of water whereby the cellulose fibers become hydrated.

Various supplementary ingredients such as the fillers, sizes, dyes, pigments and the like are also usually incorporated with the fibers in the beater engine. Treated pulp from the beater engine is then usually passed to a stock chest in which it is agitated to maintain a uniform suspension and from which it is fed to the head box of the paper-making machine. Occasionally supplementary material may be added to the stock in the head box. From this head box the treated pulp is spread on the wire and made into the paper sheet itself. The manufacture of news print and the like varies slightly in that the pulp fed to the paper machine comprises small pieces of uncooked, groundwood fibers mixed with a small proportion of hydrated cellulose fibers. Usually only enough cellulose fibers are used to bind the whole together when made into the final sheet.

Throughout the pulp- and paper-making process, therefore, a number of working steps are carried out which produce waste waters of varying content. In the pulp making process these result from the various washing steps to which the pulp is being subjected. The primary loss, however, occurs as waste water from the paper machine itself due to the material carried from the

machine by the water that is removed in converting the pulp suspension into a sheet. These waters are not only rich in hydrated cellulose fiber which has been carefully prepared by an expensive process but also contain the fillers, sizes, pigments and the like which also represent an appreciable loss.

The collection and recovery of the fibers and other materials in these waste waters is necessary for a number of reasons: because of the economic value of the fibers and fillers themselves; because the discharge of these contaminated waters presents a very serious disposal problem which in many places is regulated by law; and because in many locations the clarification of the water for reuse is a practical necessity. Accordingly, a great deal of work has been done in the past in attempting to set up processes which will effect an economical and substantially complete removal of the solids suspended in these waste waters.

Not only is it desirable to be able to recover the material contained in the waste waters from any particular machine working on a specified type of stock, but it is also often desirable to recover the fillers and fibers separately. Particularly is this true when expensive fillers, such as certain processed clays, titanium dioxide and the like which have a very real value in themselves, have been used.

Most paper mills make some attempt to clarify these waste waters. For this purpose, various combinations of apparatus have been proposed and tried. These usually take the form of a vacuum or gravity filter with or without one or more settling tanks of some form. These machines are usually quite expensive, difficult to install and, particularly in the case of settling tanks, take up a large amount of room. Frequently, therefore, all the waste material from the paper machine is passed to this recovery system regardless of the varying type of stock which may be run at intervals on the paper machine. Most paper mills also have more than one paper machine and these are usually operating on different types or colors of stock but the recovery or saveall system is often common to all the machines.

In some cases these types of apparatus have been replaced or supplemented by various equipment operating more or less on the principle of froth flotation. Most of these however, have been of the pneumatic type and all of them have been based on a non-selective flotation idea, the primary purpose being to float as large a propor-

tion of the total solid content of the waters as possible.

These previously used procedures have made fairly good recoveries of the total solid contents in the waste waters, thus partially solving the waste-disposal problem. However, from the economical point of view these systems have not been wholly satisfactory. Often as much as one-third of the material has continued to be lost. In addition to this, the material recovered has generally been of mixed grade and color so that it has little value for reuse and the prior art has not developed a satisfactory procedure adapted to separately recover the fillers and fibers.

The object of the present invention therefore is to develop a procedure adapted not only to recover substantially all the total solid content of the waste waters but also to recover the pulp in unmixed condition so that it is suitable for immediate reuse, and capable of separating the fiber and filler. These are all problems left unsolved by the prior art. In general this is accomplished by the use of a two-stage froth flotation using the necessary reagents to insure a high recovery of total solids by selectively recovering first the filler and then the fiber content of the waste waters. The present invention is primarily concerned with waste waters from the paper making machine but so far as the fibers are concerned is equally applicable to waste waters produced in various preceding steps in the manufacture of pulp.

It is an advantage of the present invention that it is not necessarily limited to any particular type of flotation machine. As was pointed out, apparatus which worked more or less on the froth flotation principle, particularly those of a pneumatic type have been used in the past in treating paper mill waste waters but none of these was operated in stages, recovering first the filler and then the fiber as in the present process. Properly operated, any good flotation machine can be satisfactorily used in the present process. I have found, however, that machines which embody a combination of mechanical agitation and aeration are most suitable for the processes of the present invention. In the development work of the present process it was found that excellent results were obtained by using a Fagergren flotation machine.

In the present specification and claims, the term "two-stage" flotation has been used only to designate a process in which first the filler and then the fiber are recovered. The term is not meant as a limitation either on the arrangement of the equipment or the number of flotation cells. The process may be used either with batch feed or as a continuous recovery. For example, a simple cell may be used to carry out both "stages" by storing the effluent water between passes. On the other hand, two cells may be used in a string to carry out a continuous recovery. Or more than one cell can be used to carry out either stage, whether in a series hookup with using continuous feed or repassing the effluent through the same cells using a batch feed. Similarly a plurality of cells in parallel may be used to carry out either or both "stages" of the process. The number of cells used and their arrangement is dependent upon such considerations as the nature and volume of waste water to be treated, the space available, the equipment available, etc. Neither the number nor arrangement of cells is a limitation on the present process.

It is also an advantage of the present invention

that it is not necessarily limited to the use of any particular froth flotation reagents. In my co-pending application Serial No. 387,067 filed April 5, 1941, I have shown that superior results with many types of pulp are obtained by using an ammoniated-talloe soap where the object is solely to remove as large a proportion of the total solid contents as possible. However, since the principal object of the present invention as pointed out above, is to recover the fibers and fillers separately, other reagents such as black liquor soap, alkali soaps, glues, saponifiable and/or non-saponifiable oils, frothers and the like may be useful. The particular choice of reagent will depend wholly upon the nature of the waste water solids.

As will be noted, many of these agents such as the glues, alum and the like are commonly used for other purposes in paper making as for example in making the size. In the flotation operation, these agents may serve as conditioning agents to place the solids in a more suitable condition for froth flotation. These agents may be already present in the waste water. On the other hand, they may be added specifically for the purpose, followed by the addition of the flotation promoter itself.

As flotation promoters, the various sodium, potassium or ammonium soaps appear to give the best results. Some of these have been previously proposed in attempts to recover the pulp from white water. However, a real degree of success was not obtained until they were used in the process of the present invention, i. e., to concentrate first the filler and then the fiber.

A remarkable feature of the present invention is the action of these promoters. Whether, the filler or the fiber is being floated the best results are obtained using a soap as a collecting agent. Despite the fact that the problem requires a selective float, a soap may be used in both stages. In fact, the same agent may be equally well used in each stage. The controlling factor appears to be the addition of the proper amount of agent in each stage. For example, the optimum amount of any one soap, such as a talloe soap, will float substantially all the filler in a fiber-free condition and a second addition of the same agent can then be used to float substantially all the fiber. Yet a single addition of the combined optimum amounts of agent, in an attempt to concentrate the filler and fiber together, results in a poorer total recovery. Or, expressed in another way, by using the present process, a better total recovery can be made using much less agent than would be required for anything like an equally good recovery using the processes of the prior art.

While the preferable agents appear to be soaps of various fatty acids and resin acids and the same agents may be successfully used in both stages, the invention is not necessarily so limited. Instead of soaps, the fatty acids or resin acids themselves may be used in either or both stages. For example, the same soap might be used in both stages, or a different soap in each stage or a soap and an acid in one stage or the other may be used.

It is also a further advantage of the process that it is not limited as to the method or apparatus used in adding the agents nor as to the point in the process at which the agents are added. Any device for the addition of the agents, many of which are well-known in the ore-dressing field, may be used. The reagents may be

added either prior to or during the flotation operation as the circumstances may demand.

A great advantage of a froth flotation apparatus in treating paper mill waste waters is its comparatively small size. A two-stage apparatus such as is used in the present process can be readily set up, often times in a substantially portable form. It can therefore be used at any stage of the pulp or paper making process. For example, the fiber content of the various wash waters normally discharged in the pulp manufacture could be fed to a tank and the fiber content thereof recovered, the water reused, and the dirt passed to waste.

Again, since flotation cells of various capacities are available, flotation can be applied directly to the various wastes as they are drawn from different parts of the paper machine itself. In this way it is possible to remove the bulk of the solid content at once so that either the filler, the fiber or the water could be returned directly to use. Only the substantially clarified effluent need be sent to a subsequent filter or other system and thereby greatly reduce the load on it.

Or, as another possibility, the cells could be installed at various points in connection with any other apparatus. For example, many operating mills are equipped with both a settling tank and a vacuum filter. The flotation cell could then be installed before the settling tank, between the settling tank and the filter, or in tandem with both settling tank and filter. Or, if desired, the flotation cell could be used to replace both.

In a test on a system of this type it was found that the combined vacuum filter and settling tank recovered slightly over 70% of the total suspended solids. By the use of a two-stage flotation operating without either the filter or settling tank, a recovery of about 95% of the suspended solids was obtained when 1.0 lb./ton of an ammoniated talloel was used as a promoter.

Further tests brought out the fact that it was possible to use a smaller amount of flotation reagent and still obtain over 90% recovery of the total suspended material by carrying out the two-stage flotation in conjunction with the vacuum type filter but without the aid of the settling tanks. As the settling tanks were necessarily large in order to store a large volume of white water and thereby allow time for efficient settling, the saving of space by their elimination would have been very appreciable.

As a further procedure it was found that, by using the two-stage flotation in combination with both the vacuum filter and the settling tank, a recovery of about 99% of the total suspended material was obtained. Thus, it is indicated that the flotation process may be used in combination with equipment which already may be in service in a paper plant and frequently serve to eliminate cumbersome portions of such equipment or to improve the general efficiency of the system.

Another advantage of a froth flotation procedure is that it is quick acting so that there is no long time of residence in the machine. This is a particular advantage when the paper machine is being converted to the running of one type or color of stock to some other. With the older systems where a considerable body of waste water had to be accumulated there was a considerable lag in the change-over which resulted in the recovery of mixed grades of fibers, fillers, etc., or in mixed colors.

The invention will be described in greater detail in conjunction with the following specific

examples, which are meant to be merely illustrative and do not in any way limit the invention.

EXAMPLE 1

- 5 A sample of paper mill white water containing cellulose fibers and a clay filler was fed at the rate of 2 gals./min. to a small size Fagergren flotation machine operating at a speed of 2200 R. P. M. An alcoholic solution of ammoniated talloel in the proportion of about 0.4 lbs./ton was fed to the machine. The results are shown in the following table.

Table I

Feed, gms./l			Effluent, gms./l			Recovery, per cent		
Filler	Fiber	Total	Filler	Fiber	Total	Filler	Fiber	Total
1.00	1.20	2.20	0.15	1.15	1.30	85.0	4.2	41.0

EXAMPLE 2

- 23 The procedure of Example 1 was repeated on a sample of white water in which the filler was mainly comprised of precipitated chalk. A speed of 1500 R. P. M., feed at the rate of 2 gals./min. and an alcoholic solution of ammoniated talloel in the proportion of 0.5 lb./ton were used. The results are shown in Table II.

Table II

Feed, gms./l			Effluent, gms./l			Recovery, per cent		
Filler	Fiber	Total	Filler	Fiber	Total	Filler	Fiber	Total
0.80	1.00	1.80	0.09	0.92	1.01	88.7	8.0	56.2

EXAMPLE 3

- 45 A sample of white water containing cellulose fiber and a filler comprising principally titanium dioxide was fed at the rate of 8 gals./min. to a Fagergren flotation machine operating at a speed of 1900 R. P. M. An alcoholic solution of ammoniated talloel in the proportion of about 0.7 lb./ton was used. The results are shown in Table III.

Table III

Feed, gms./l			Effluent, gms./l			Recovery, per cent		
Filler	Fiber	Total	Filler	Fiber	Total	Filler	Fiber	Total
0.40	0.60	1.00	0.05	0.59	0.64	87.5	1.7	34.0

- 60 In the preceding examples it will be noted that an excellent recovery of the filler in a comparatively fiber-free condition has been made. However, the total solids removed was not particularly high. Since this would not solve the problem of waste disposal or water clarification and since the fibers themselves also have a very appreciable value, the effluent from the filler recovery was treated to recover the fibers. This procedure will be illustrated in the following examples.

EXAMPLE 4

- 70 A white water sample similar to that of Example 1 was given a two-stage flotation in which the first machine was operated at 1500 R. P. M. and the second at 1900 R. P. M. 0.8 lb./ton of ammoniated talloel was used in the first machine and 0.2 lb./ton in the second. Using a feed rate

of 2 gals./min. an excellent recovery was obtained. Results are shown in Table IV.

Table IV

Feed, gms./l			Effluent, gms./l			Recovery, per cent		
Filler	Fiber	Total	Filler	Fiber	Total	Filler	Fiber	Total
0.80	1.20	2.00	0.02	0.10	0.12	97.5	91.6	94.0

EXAMPLE 5

A white water sample similar to that of Example 2 was given a two-stage flotation at the rate of 2 gals./min. Each machine was operated at 1500 R. P. M. and 0.5 lb./ton of ammoniated talloel was used as a reagent in each stage. The results are shown in Table V.

Table V

Feed, gms./l			Effluent, gms./l			Recovery, per cent		
Filler	Fiber	Total	Filler	Fiber	Total	Filler	Fiber	Total
0.80	1.00	1.80	0.03	0.05	0.08	96.3	95.0	95.6

EXAMPLE 6

A white water sample similar to that for Example 3 was fed at the rate of 2 gals./min. to a two-stage flotation operation in which the first machine operated at the rate of 1900 R. P. M. and the second at 1500 R. P. M. 0.2 lb./ton of ammoniated talloel was used in the first stage and 0.3 lb./ton in the second stage. Results are shown in Table VI.

Table VI

Feed, gms./l			Effluent, gms./l			Recovery, per cent		
Filler	Fiber	Total	Filler	Fiber	Total	Filler	Fiber	Total
0.17	0.25	0.42	0.004	0.009	0.013	97.5	96.5	96.9

Thus, the above examples indicate that high recovery of either filler or fiber, each relatively free of the other, is possible by the use of the process of the present invention. Also, it is demonstrated that water showing a high degree of clarity and suitable for paper making operations

is also obtained. Thus, the overall efficiency of the process is very high.

It also should be noted in connection with Examples 4-6 that in those cases where the last small fraction of solids must be removed, the effluent from the last flotation cell can be passed to a settling and/or filtering system. These latter would then be able to be operated at high efficiency since the major portion of the load which they would have to carry has been taken up by the flotation machines.

I claim:

1. A method of clarifying paper mill waste waters and recovering the filler and fiber content thereof which comprises subjecting said waste waters to a froth flotation in the presence of only a sufficient amount of a promoter selected from the group consisting of higher fatty acids, rosin acids, talloel, the sodium, potassium and ammonium soaps thereof and black liquor soap to selectively float the filler in a substantially fiber-free condition, said promoter being capable of floating both fiber and filler when present in larger amounts, collecting the resultant concentrated filler and subjecting the residual material to a froth flotation in the presence of a sufficient amount of a promoter selected from the same group to concentrate fibers.

2. A method according to claim 1 in which the same promoter is used in each stage.

3. A method according to claim 1 in which ammoniated talloel is used as a promoter in each stage.

4. A method of clarifying paper mill waste waters and recovering the filler and fiber content thereof which comprises subjecting said waste waters to a two-stage froth flotation in the presence of a promoter selected from the group consisting of the higher fatty acids, rosin acids, talloel, the sodium, potassium and ammonium soaps thereof and black liquor soap, said promoter being capable of concurrently floating a portion of both filler and fiber when present in sufficient quantity, the quantity of promoter used in said first stage being large enough to float substantially all the filler in a substantially fiber-free condition but less than the amount required to float a substantial amount of fiber with said filler.

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