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The Factors Governing the Retention of Emulsified Elastomers Added to Pulp in the Beater

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By Raymond Wagner

The term "elastomer" applies to that group of substances which has the property to retain their original shape within the elongation limits at ordinary temperatures. This group can be divided in two general divisions - natural and synthetic rubbers. Crude rubber is the product of the tree, Hevea brasilieusis (8), believed to be a natural polymerization product of isoprene. Synthetic rubbers are emulsified polymers produced artificially and possessing the properties similar to those of natural rubber. The word "synthetic" might be termed as a misnomer here since an exact duplicate has not been formulated conforming to the structure of natural rubber. Although natural rubber has a more versatile use the synthetic rubbers can be formulated to meet the definite demands of an end product. An aqueous dispersion of these polymers is referred to as a "latex".

The synthetic rubbers of commercial and experimental value as use in beater additives of pulp are as follows (10):

1. Chloroprene - a chloro-butadiene polymer sold commercially as Neoprene, GR-M and others.

2. Styrene-Putadiene - a copolymer sold commercially as Buna S, GR-S and Chemigum, Dow 512-K and others.

3. Butadiene-Acrylonitrile - a copolymer sold as Buna N, Hycar, Chemigum N, ëtc..

4. Isobutylene-Isoprene - a copolymer sold as Butyl, GR-I, Flexon, etc..

A number of previous investigations have shown that

elastomers incorporated in the pulp gives improved strength characteristics without any noticeable effect on the appearance of the paper. Since latices are added in dispersions of very small particle size, we are confronted with the factors governing the retention of these additives to produce a higher quality paper at an economical cost.

Tracing through the factors in the order of sequence in usual mill operations, our first problem is the condition in which the latex should be added to the beater and in what sequence of beater furnishing it should be added.

As early as 1925, Hopkinson and Rose (3) took out a patent on rubberizing paper in the following matter. An alkali-treated latex is added to a hydrated pulp which has been alkaline treated and beating is continued until the latex has been thoroughly mixed in the pulp. A coagulating agent having an acid reaction is then added in a dilute solution, two thirds of which is added at first, followed by thorough mixing, and then the remainder of the precipitating agent is added. Addition by this method tends to prevent excessive localized action of the acid on the latex which would thus form an agglomerated mass of latex with poor deposition on the fiber, whereas, if added in portions as described, the precipitating action would be more uniformly distributed in the beater and the portion added last would act as a stabilizing agent, producing a better fiber-latex bond. Most all authors agree that the best distribution and most effective results are obtained when latex

is furnished to the beater at a solids content from less than one per cent, up to five per cent (4).

A survey was recently cited by C. G. Landis (5) on the various processes used in beater addition of latices. Three processes were described which were of major importance - the Neoprene Latex Process - the Snyder Process - and the Bardac Process. The Neoprene Process consists of adding a stabilizing agent to the latex in the pulp, plus a sensitizing agent such as alum, controlling the pH on the alkaline side, to obtain maximum deposition. In the Snyder Process the latex is added to the pulp followed by a special phenolic resin and acidified alum. The Bardac Process is more of a complicated process which requires more time and attention than the ones previously mentioned. Pulp is pretreated with a melamine-resin and allowed to age a short time, after which emulsions of a latex containing a special anionic dispersing agent can be added and deposition of the latex on the fiber takes place immediately.

Landes (5) also mentions the use of polyester elastomers, phenolic elastomers, and incorporation of elastomers in pulp containing polyvinyl chloride and acetate, producing papers which retain their flexure properties.

The effects of adding a latex at different phases in the beating cycle, was proven by Yosé and Aiken (10), that the best results were obtainable when the latex was added after the beating cycle, followed by coagulation with alum. Experiments were carried out in a standard laboratory beater in the following

sequence:

(a) Beat pulp, add latex, add alum.

(b) Add latex, beat pulp, add alum.

(c) Add latex, add alum, beat pulp.

(d) Beat pulp, add alum, add latex.

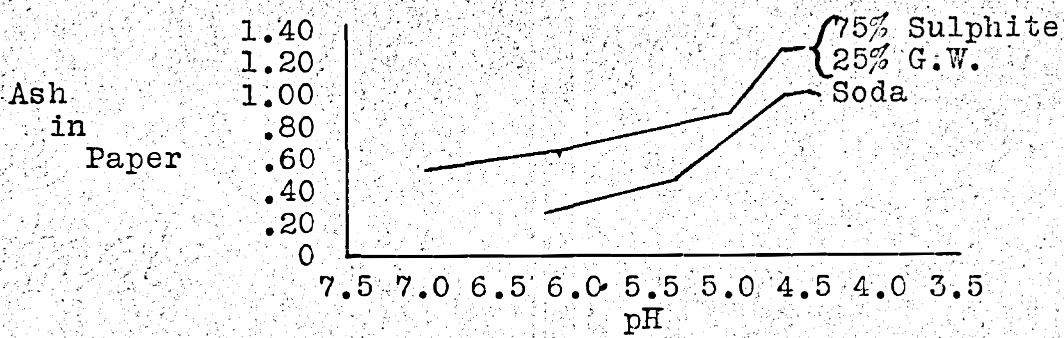
When the latex was added to an unbeaten pulp and followed by the addition of alum, the latex coagulated to form large lumps of rubber. When the same substantial amount of latex was added to a beaten pulp the coagulation was uniform without any undesirable lump formations. This phenomena was believed to be due to the large surface area of the beaten pulp, which allowed the latex to be precipitated on the fiber. Agglomeration of the latex also appeared when the alum preceded the latex addition. This would thus be due to localized action of the alum, precipitating the latex before it had the chance to come in contact with the fiber.

This particular phase was given more thorough investigation by Oliner and O'Neil (6), who studied the fiber-latex bond during different stages of the beating cycle. Their work pointed out that resin retention increases at a high rate during the early stages of beating. As beating proceeds, the resin retention rate, and therefore, the number of bonds due to resin become almost constant. As beating continues, the fiber-resin-fiber bonds, in the total number of bonds, decreases. As beating still proceeds, the total number of bonds increases and the amount of resin retained at the end of the cycle is practically

constant.

One might assume that the strength of this bond is substantiated by the addition of the floculating, or "setting" agent. In choosing a floculating agent, consideration must be given to the charge of the existing cation. A compound whose charge of the cation and the anion is of maximum magnitude when ionized, provides the requirements necessary to precipitate a filler, which we may consider here to be latex, onto the fiber, to obtain the maximum bonding force, maintaining better retention of the filler added in the final product. For economical purposes, papermakers alum can be used most advantageously, since the Al ion posesses a valence of positive three and the sulphate ion of negative two, when ionization occurs. The aluminum ion now serves as a bonding media between the negatively charged cellulose and the latex filler. Another function of the alum is that it precipitates the soap film, that most latices are stabilized with, depositing the latex on the fiber. Sodium silicate also aids in filler retention, if added early in the beating cycle. Three reactions occur when silicate is introduced into the beater - hydration is aided - forms a precipitate with alum - affects dispersion and subsequent retention due to the gelatinous nature of the silica. For maximum precipitation of silica the pH must be carefully controlled by addition of alum to operate at a pH of 4.5. An anology showing the effect of sodium silicate and alum in paper stock on the retention of the filler added is plotted on the following graph from Witham's, "Modern Pulp and Paper Making" (9)

Ash is plotted against pH, the ash which is characterized by the retention of the filler.



Surface active agents of anionic, cationic, and non-ionic nature are now obtainable which are very substantive to cellulose and function effectively as dispersing and wetting agents which is of importance in obtaining a uniform deposition of latex on the fiber.

Cationic latices (2) are now being formulated which have a direct affinity for cellulose, certain types of which are said to be 100% retainable. Latices of this type are attracted to the negatively charged cellulose and within ten to fifteen minutes complete deposition takes place.

Yost and Aiken (10) found that it was not necessary to reduce the consistency of the pulp if the amount of latex incorporated in the pulp was less than 33%. However, if 50% or more latex is furnished they advise dilution of 3% consistency.

The type of pulp used seem to be of some significance in the retention of the latex. Unbleached pulps appear to be slightly favored for the amount of latex that can be incorporated into the pulp. Perhaps this would be due to one or more compounds associated with the unbleached fiber, as was discovered

by Bursztyn (1) in his work on the retention of thermosetting urea resins.

The same factors governing retention apply to pulp containing latex, as to an ordinary furnished pulp, in respect to basis weight, pH, and paper-machine operation.

Retention is improved with an increased basis weight up to a certain point at which it starts decreasing (7).

Factors to be considered for proper retention in paper machine operation are length of wire, design of inlet and its effect of depositing the first layer of fibers, shake, vacuum on suction boxes and rolls, and the speed of the machine.

In the work of Yost and Aiken (9) using a butadiene-acrylonitrile polymer, there was no effect on the drainage rate when latex was incorporated into the pulp. pH was kept between 4.5 to 5.5 to obtain optimum properties. A pH above 6.5 tended to produce a sticky sheet. To determine whether the pH or amount of alum affected the retention, a series of experiments were run keeping the amount of alum constant and varying the pH by adding sodium hydroxide. Highest results were obtainable at a pH value between 5.3 and 6.9 rather than at 4.5. Following this, a series of experiments were conducted using different alum/sodium hydroxide mixtures. A pH range of 5.5 to 6.5 gave the optimum results in this series, which seemed to be superior to all the other series.

In summarizing it will be noted that retention may be based upon three main factors (1) cofloculation (2) mechanical attachment and (3) filtration. Cofloculation results as the action

of the interfacial walls between the fiber and the latex and between the individual latex particles. Retention by mechanical attachment is that retention due to the wedging of the filler into the imperfections of the fiber wall and imbedding of the filler in a gelatinous or plastic substance which in turn is retained on the fiber. Retention by filtration is simply the retaining of particles which are larger then the interstices between the individual fibers, when a fiber mat is being formed on the wire.

Beater addition of elastomers should be of increasing importance in the paper industry since it involves on the inexpensive materials being used in paper manufacturing. Very few changes would be required in the actual mill practice to obtain a higher quality sheet economically.

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EXPERIMENTATION

From the study of literature on the factors concerning retention of emulsified elastomers the following variables were considered of prime importance.

1. Type of pulp
2. pH of beater stock at time of addition
3. Basis weight of sheet formed
4. Freeness of pulp
5. Sequence of addition to pulp
6. Final pH adjustment
7. Time of contact
8. Other beater additives (wetting agents, etc.)
9. Alumina concentration.

In this experimentation the variables were limited to a final pH adjustment and speceial additives. Freeness was maintained a variable only in the initial series since observations showed only slight effects on the treated pulp.

For the puppose of this experiment three commercial latices available as beater additives was used:

1. 512K - a styrene-butadiene copolymer
2. Geon - a polyvinyl chloride
3. Kralastic 4109 - a special emulsion of unknown composition.

Initial samples were 100g. portions of a West Coast bleached sulphyte pulp in a 2% slurry. Samples were treated and agitated in 8 oz. wide mouth bottles. Gang stirrers with stainless steel paddles were used for mild agitation.

Sodium hydroxide was added to the slurry to provide selected pH values after the additions of two per cent (2%) alum based on the fiber. The amount of sodium hydroxide added was based on titration curves of the pulp - latex - alum slurry. Latex diluted to a 2% dispersion was added to supply 10% latex solids based on the fiber. 2% alum was added to precipitate the latex. This was followed by 15 minutes of agitation on the gang stirrers.

Another series was made using a cationic wetting agent. In this series the amount of wetting agent was held constant and alum was added to adjust to a pH of 4.5, 5.5, and 6.5.

Microscopic slides were prepared so that a visual comparison of the most efficient means of deposition of the latex on the fiber could be made.

Beater runs were then made following procedures which gave optimum results as observed under the microscope.

Pulp was beaten at a consistency of 1.96% to a freeness of 300 10 ml. measured on a Canadian Standard Freeness tester.

Standard 2.5 g. sheets were made with the treated pulp on the Noble and Wood sheet machine.

EXPERIMENTAL RESULTS

pH values were taken and microscopic slides were prepared on the initial samples to observe the following conditions.

1. Precipetation of latex
2. Relative size of agglamerated particles, if any
3. Amount of latex deposited on the fiber or fibrils

Optimum conditions were considered to prevail when the maximum amount of latex of the smallest particles or agglamerate size was deposited along the body or on the fibriles of the fiber.

The initial samples of 100g portions of a 2% slurry were run and designated by series A. B. C. D. Beater runs followed identified by series E. F. G. & H.

The sequence of operations after pulp disintegration were

1. NaOH addition
2. five minutes agitation
3. latex addition
4. five minutes agitation
5. alum addition.

In series A Geon and 512K latex was added to alkaline treated pulp samples that contained sufficient amounts of NaOH to provide pH values of 4.5, 5.5, and 6.5 after the final addition of alum was added to furnish 2% alum based on air dried fiber.

In series B the NaOH addition was replaced by the addition of Nopcogen 14-L, a cationic wetting agent of a lauric derivative. The wetting agent was held constant in this series providing 1% Nopcogen based on air dried fiber. The latex addition was followed by the wetting agent using the same latices as in series A. Alum was added in sufficient amounts to adjust the pH values to 4.5, 5.5, and 6.5 respectfully.

Series C & D was run identical with series A & B respecfully using Kralastic latex 4109.

Microscopic observations of series A showed no substantial

bonding of the latex to the main body of the fiber but rather to the smaller fibrilated parts and the small fiber segments of the fiber that were broken off in the beating and agitation process. Dow 512K appeared to precipitate in larger agglomerates in all cases than did Geon. Deposition appeared to be the most substantial at a pH valve of 6.5.

The latex in series B was not as well bonded as in series A, however, the pH range between 6 and 6.5 seemed to give the most favorable results with fairly small agglamerates held loosely on the fibrils. Large agglamerates resulted in the lower pH range with less deposition. The same held true when the cationic wetting agent was added to Kralastic 4109 in series D.

Series C showed more favorable results than the other series with good deposition of the latex on the fibrils and the small cut segments of the fiber. Maximum deposition occured at a pH of 5.1 in which case no NaOH was added before the latex addition.

The Kralestic treated pulp showed much better deposition of the latex on the fiber after an aging period. This condition appeared to exist independent of the pH values that were tested. The white water above the settled suspension of fibers was clear in all cases. This phenomenon was not studied further due to limitation of available time.

Assuming that optimum conditions prevailed when the deposition of the latex occurred in small particle size along

the body of the fiber subsequent beater runs were made.

The type of latices were limited to the polyvinyl chloride and the special emulsion of unknown composition which showed promising results. The pH was adjusted to betweetn 6.5 and 7.0. The latex was added to supply 10% latex solids based on the fiber followed by runs furnishing 3% latex based on the fiber.

The sequence of operations after the beating cycle were,

1. NaOH addition
2. five minutes agitation
3. latex addition
4. five minutes agitation
5. alum addition.

Alum was added to furnish 2.7% solids based on fiber compared to 2.0% on the 100G. Samples in series A and C. This was due to graphical interperations which was carried out on a small samples that were not characteristic of the larger portions of constituents furnished and of the larger volume of Kalamazoo City Water which is highly alkaline.

Four beater runs were made designated as series E F G & H. In series E and F 10% Geon and Kralastic 4109 latex was added respectfully followed by G & H of 3% latex addition of the two above latices.

Handsheets were made from the treated pulp and extracted with xyline in Soxleth extractors to determine per cent retention of latex.

Due to improper selection of the solvent or to improper technique in sheet formation the figures obtained from the

extractions produced no conclusive evidence that I feel could be reproducible.

However, from the microscopic observations of the samples, it is evident that maximum precipitation of the latex on the fiber is obtained at a pH range from 6.0 to 7.0.

The Kralastic latex showed the most favorable results and furbher investigation of the alumina concentration in a pulp-latex system should prove to bery interesting.

From limited observations the aging effect also appears to be an important factor governigg the precipitation and retention of emulsified elastomers.