

# A new concept of chemistry refining processes

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**ABSTRACT** *In the SCHL (structural changes in hydration layers) theory, refining is characterized by determining the "hydration factor." This factor is an evaluation of the influence of water-soluble hydrated substance in hydration forces. The hydration factor allows us to estimate both the qualitative and quantitative influence of various substances in water on the consumption of beating energy. A semi-quantitative proof for the existence of these hydration forces is described.*

## KEYWORDS

Chemical analysis  
Hydrogen bonds  
Pulping  
Refining

In pulp beating, not only does mechanical action take place, but so does chemical action. However, the medium in which beating takes place—usually water or dilute aqueous solutions—does not treat the mechanically disintegrated fibers in the pulp in a classic chemical way. That is, the aqueous medium does not change the composition and structure of molecules forming individual pulp fibrils and microfibrils.

What is being changed is the composition of the phase interface between the pulp and water medium and the molecule arrangement in single pulp formations, especially in places with simultaneous mechanical action. In other words, the beating process entails chemical changes in pulp above the level of the basic molecular structure.

Such a process is not only connected with the increase of the specific surface of pulp fibers, but it has a more complex nature. As beating increases, the content of hydrophilic groups, especially hydroxyl groups in polysaccharide fibrous pulp material, is increased. The result is increased hydration, which leads to deterioration of the drainage process.

Theoretically, so-called "chemical beating aids" work because the fi-

brous surface of pulp can be activated by the adsorption of hydrophilic polymer substances. These substances contain a lot of groups that can accept H-bonds (such as -OH and -NH<sub>2</sub>). With free or beaten stock, these aids change the drainage characteristics of the stock and therefore the mechanical properties of the paper made from it. (Drainage gets slower, and paper strength increases.)

These aids do not directly affect beating itself, neither do they interfere with it. They only change the properties of the product, making the pulp behave as if it were beaten more thoroughly. Such aids can be called "pseudo-beating aids." Starches, glucomananes, manogalactanes, and others (1, 2) can be included in this group.

On the other hand, there are substances that, in beaten or free pulp suspension, neither change drainage properties nor influence the strength properties of the paper made from pulp. Nevertheless, they accelerate the effects of beating and refining though the operating load of the refiner is held constant. These substances that act directly as beating aids are mostly low-molecular-weight compounds of various colored materials of the Congo Red type (3-4) and others (5, 6).

Finally, there are compounds that both intensify the refining process and influence the drainage properties of paper stock by aiding the retention of filler and other paper stock constituents, which influence the strength properties of paper (7-8). These compounds are high-molecular-weight compounds of different composition containing strong hydrophilic groups (carboxylic, amide, nitric groups, etc.). Many of these substances are made from waste materials: waste fibers separated from the mercerization liquor in the production of regenerated fibers, modified secondary fibers, etc. (7). These beating aids are classified as shown in Table I (9).

The common features for all beating aids are that they are hydrophilic and that they adsorb onto cellulose. The effect of pseudo-beating aids is relatively simple to explain. The action of these aids is based on the activation of the surface of pulp fibers. The fiber surfaces can be activated when suitable hydrophilic substances containing convenient (mostly hydroxyl) groups are adsorbed on the surface of pulp fibers. In this way, the number of hydrated hydrophilic groups on a surface unit of fiber formations increases, achieving the same effect as in beating. This effect

is like that of mixing free stock with fine, strongly swelled stock (9).

But in what way do direct or complex beating aids accelerate the refining process? Is defibrillation accelerated by changes in the electrokinetical behavior of the system, especially when more hydration of the fibers takes place when beating is relatively slow?

Obviously, the phenomenon cannot be explained on the basis of zeta potential. The zeta potential pertains to the relative motion of the phase interface, which is quite wide within swelled fibers and is consequently immovable in the interfibrillary fiber system. That is why electrostatic activity caused by electrokinetic phenomena affixes to interactions of fiber formations, especially in diluted fiber suspensions.

What kinds of physical forces are holding all the hydrated fibrillar system together that, being properly influenced, make defibrillation easier? The concept of increased osmotic pressure caused by the local concentration of the beating aid on cellulose surfaces (6) implies several possibilities. It is not clear, besides, how such a large molecule as a beating-aid molecule could get into the closed fibrillar space of wood fibers. The answers to these questions should be searched for in the behavior of such highly hydrated hydrophilic systems.

The DLVO theory (10-12) is used for describing the interactions of lyophilic surfaces in water media and is based on the van der Waals and electrostatic forces determined as zeta potential. However, this theory does not suit hydrated hydrophilic systems (13). Although the DLVO theory also accounts for bonds other than those only developed by van der Waals forces (e.g., hydrogen bonds), the distances at which interacting surfaces are found in the beating process are too small for electrostatic forces to act and too large to form hydrogen bonds. Therefore, the SCHL (structural changes in hydration layers) theory has recently been designed to deal with the interaction mechanism in hydrated hydrophilic systems.

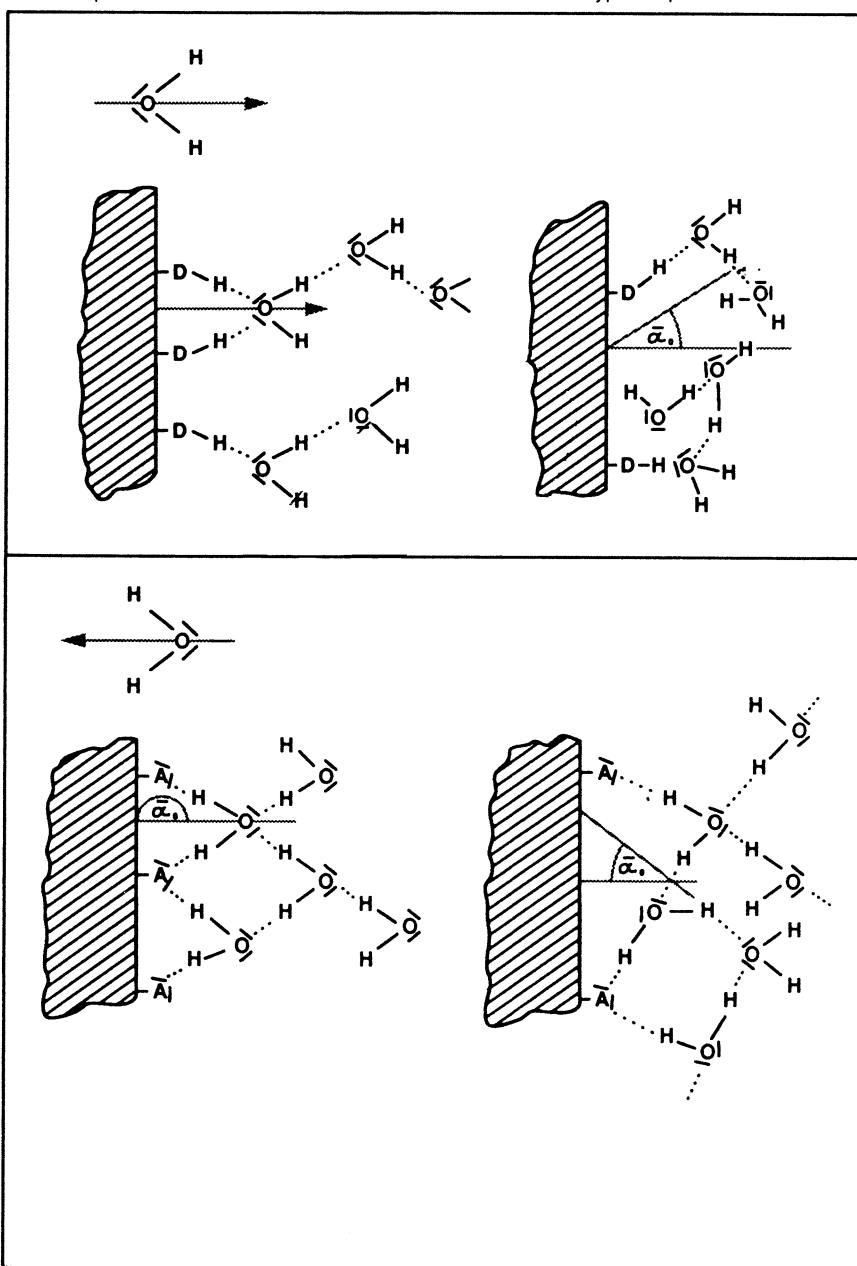
### Principles of the SCHL theory

The SCHL theory (14-15) is based on the dipole nature of water molecules and on their two possible orientations in hydration spheres (Fig. 1):

### I. Classification of chemical beating aids

	Beating aids		
	Pseudo	Direct	Complex
Effect	Strength Drainage retention	Beating speed	Beating speed Dry strength Wet strength drainage Retention sizing
Substances	Polymers Polysaccharides	Monomers Amines Amides Dyes Other	Polymers Modified polysaccharides Polyamides Polyamines Modified lignins
Dosage	1-5% Before and after beating	0.1-1% before beating	0.5-5% before beating

### 1. Conception of the orientation of water molecules on various types of phase interfaces



1. Orientation with the hydrogen atoms of water molecules in the direction to the active surface of the fiber
2. Orientation with the oxygen atom of water molecules in the direction to the active surface of the fiber.

These two different orientations of water molecules are caused by the amphoteric nature of water molecules with regard to accepting hydrogen bonds. A water molecule has the ability to join with other molecules or groups with hydrogen bonds, in which it can act as the hydrogen atom donor or acceptor. The intermolecular field of force produced by the hydrogen bonds formed will then spread by means of the other molecules through the hydration sphere under the influence of this orientation of water molecules, becoming more and more diffused until it equals the zero value within water. This effect gives rise to forces that cause action between interacting surfaces—that is, to hydration forces.

If the water molecule orientation to each of the interacting surfaces is equal, then both surfaces will affect each other with repulsing hydration forces. On the other hand, if the orientation of water molecules is different, the two surfaces will attract. Interestingly, the repulsive forces are effective over a greater distance (Fig. 2). This difference appears in the interactions of heterogeneous surfaces in which repulsive and attractive hydration forces act simultaneously as a kind of equilibrium established in which the two surfaces reach a definite optimum distance from each other (Fig. 3). In the interaction, mutual diffusion of hydration spheres takes place, connected with a change of their structure. These structural changes are on the molecular level and should be accompanied with proper temperature effects (16, 17).

For hydration forces to originate, it is necessary for water molecules to reach a suitable orientation in hydration spheres. This orientation is determined by H-donor and H-acceptor groups, by their amount, and by the strength of the hydrogen bond formed with water, or in another term, by the value of intersurface tension  $\gamma_{i,s}$ . All hydrated systems with a high specific surface behave in this manner. These

include various porous systems filled with water and its solutions, gels, quasi-gelous systems, etc. According to this theory, the groups forming hydrogen bonds with water can be divided into three types:

- H-donor groups and molecules: such as primary alcoholic OH-groups, secondary amino groups in aliphatic compounds, and primary amino groups partially
- Amphoteric groups and molecules: such as H<sub>2</sub>O, secondary alcoholic OH-groups in polysaccharides, and partially primary amino groups, amido groups, etc.
- H-acceptor groups: such as hemiacetal oxygen in saccharides, carbonyl groups, and tertiary amino groups.

The behavior of these groups depends considerably upon surrounding groups that are not necessarily linked up to H-bonds. For example, surrounding groups having the -I effect will intensify the donor nature of oxygen in these groups. The mesomeric effect has the opposite influence: the hydroxyl groups will strengthen their acceptor nature and weaken the donor one (15).

In this context, these forces do not lead to qualitative chemical changes of interacting molecules but only to changes in their arrangement and their orientation in the system. We are discussing them as interactions that occur above the level of basic molecular structure and that lead to chemical changes that do not alter the basic molecule. The functioning of different types of forces depends on distance. As shown in Fig. 4, the shortest distances are in forces connected with chemical bonds. H-bonds follow. Finally, colloidal (physical) forces occur in interactions above the molecular structure, such as those interactions characterized by van der Waals, hydration, and electrostatic forces.

However, the effect of different forces depends not only on distance but also on mutual acceptability. For example, London's dispersion forces can accept only nonpolar hydrophobic molecules or groups, while hydrogen bonds can merely form molecules having corresponding polar hydrophilic groups. The action of hydration forces depends strongly upon temperature. The effects of hydration forces

quickly disappear with rising temperatures.

### **Pulp beating: aspects above the molecular level**

The purpose of beating is to disintegrate the above-molecular structure of pulp fibers to a maximum extent with minimum destruction of macromolecular cellulose chains. The above-molecular structure of cellulose as the main pulp constituent is formed by an abundant system of hydrogen bonds holding together separate cellulose chains and their segments in more or less oriented zones. The cellulose molecule is wound to a helix, owing to intramolecular and intermolecular H-bonds, to form the fiber structure of an elementary fibril. These elementary fibrils are joined into microfibrils forming the fibrillar pulp system (18) together with other constituents of polysaccharide and lignin origin.

Main H-bond types forming above the molecular cellulose structure, such as follow from structural space models, are presented in the appendix. Intramolecular H-bonds are formed either between different planes or on the same plane in which separate cellulose chains are found that occupy the most advantageous so-called "C1" conformation (19). We further suppose that hydrogen atoms linked to carbon atoms in axial positions give rise to nonpolar spheres in cellulose matter. These nonpolar spheres make it difficult for water molecules to gain access to formed H-bonds, when H-bonds are being destroyed (20).

Destroying the H-bonds with water and its solutions will depend not only on their strength but also on the nature of the H-bonds. The destruction can be reversible or irreversible. Those H-bonds produced from amphoteric groups are usually reversible H-bonds, while the groups of donor or acceptor nature usually form the irreversible H-bonds. Thus, two or three types of qualitatively different H-bonds can be distinguished (15), following the scheme presented in the appendix :

1. H-bonds of irreversible nature:
  - Glycosidic oxygen: hydrogen atoms of several hydroxyl groups, such as C'(6)OH-O(linking)
  - Hemiacetal oxygen: hydrogen

- atoms of several hydroxyl groups, such as C'(3)OH-O(ring), C'(2)OH-O(ring), and C'(6)OH-O(ring)
2. Reversible H-bonds between amphoteric primary and secondary hydroxyl groups: C'(2)OH-C(3)OH and C'(6)OH-C(6)OH
  3. Slightly irreversible type: between primary and secondary hydroxyl groups, such as C'(6)OH-C(2)OH.

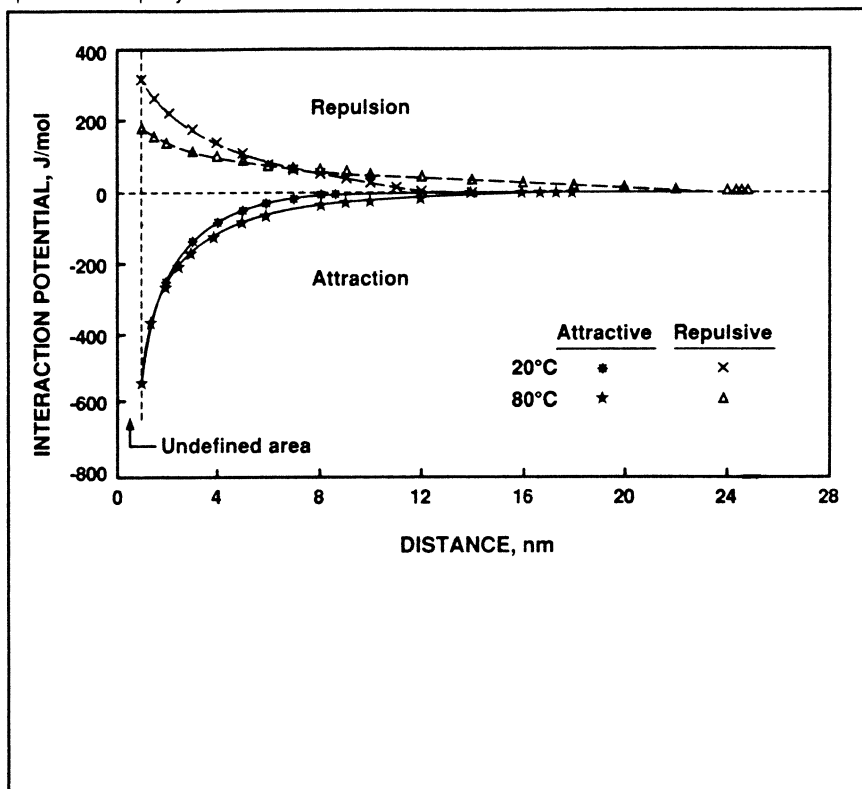
These qualitatively different H-bonds then cause oriented (crystalline), less oriented, and unoriented (amorphous) zones to occur in native cellulose. Transitions among these portions are not smooth, but the orientation and the degree of coherence in various parts of the fiber differ. There can exist different arrangements even in oriented zones. [Three arrangements of oriented portions are usually distinguished (21).] Water causes cellulose to swell but not to dissolve. The reason can be that strong hydrogen bonds exist in oriented zones. This does not mean, however, as some experimental observations show (22), that water molecules would not come into contact with several hydroxyl cellulose groups in oriented zones. It is possible, and it logically follows from the SCHL theory as well, that water molecules can penetrate into the oriented cellulose zones without causing any substantial changes.

### Mechanism for the aqueous destruction of H-bond systems

In this mechanism (9, 15), water molecules first destroy the H-bonds of reversible nature in such a way that these water molecules are oriented to each of the surfaces in like manner. Both the surfaces then become affected with relatively strong repulsive hydration forces. The strengths of these forces are determined by the amount and size of these centers relative to the total area of destroyed surfaces.

As mentioned, the repulsing effects of these forces extend over larger distances than the effects of attractive forces. Consequently, they penetrate like a kind of wedge between irreversible H-bonds to destroy them, which does not mean that the attractive action evoked by them is lost. In this mechanism, by contrast, water molecules are oriented to each of the surfaces mostly in the opposite direc-

2. Dependence of interaction potentials upon the distance of interacting homogeneous and quantitative equally flat formations



tion. For this reason, attractive forces result between them to prevent the surfaces from drawing further away. The interaction of these repulsive and attractive forces results in a kind of equilibrium that maintains the two surfaces at certain distances, separated by hydration spheres of various widths. In practice, this action is called "swelling." Further action of repulsive hydration forces or of outer forces, such as produced by mechanical beating, may lead to their full removal and to the stabilization of this process—for instance, with diluting.

A possibility for facilitating the disintegration of the H-bond system in pulp beating is to use substances that carry some groups on their surfaces that are evenly arranged in space (or are arranged in another suitable way from the view of the geometric arrangement of the bond system in H-bonds to be destroyed). These substances are able to accept H-bonds that are qualitatively coincident with water. This includes such groups that maintain or cause the coincident orientation of the bound water molecules surrounding them. Figure 5 presents this mechanism.

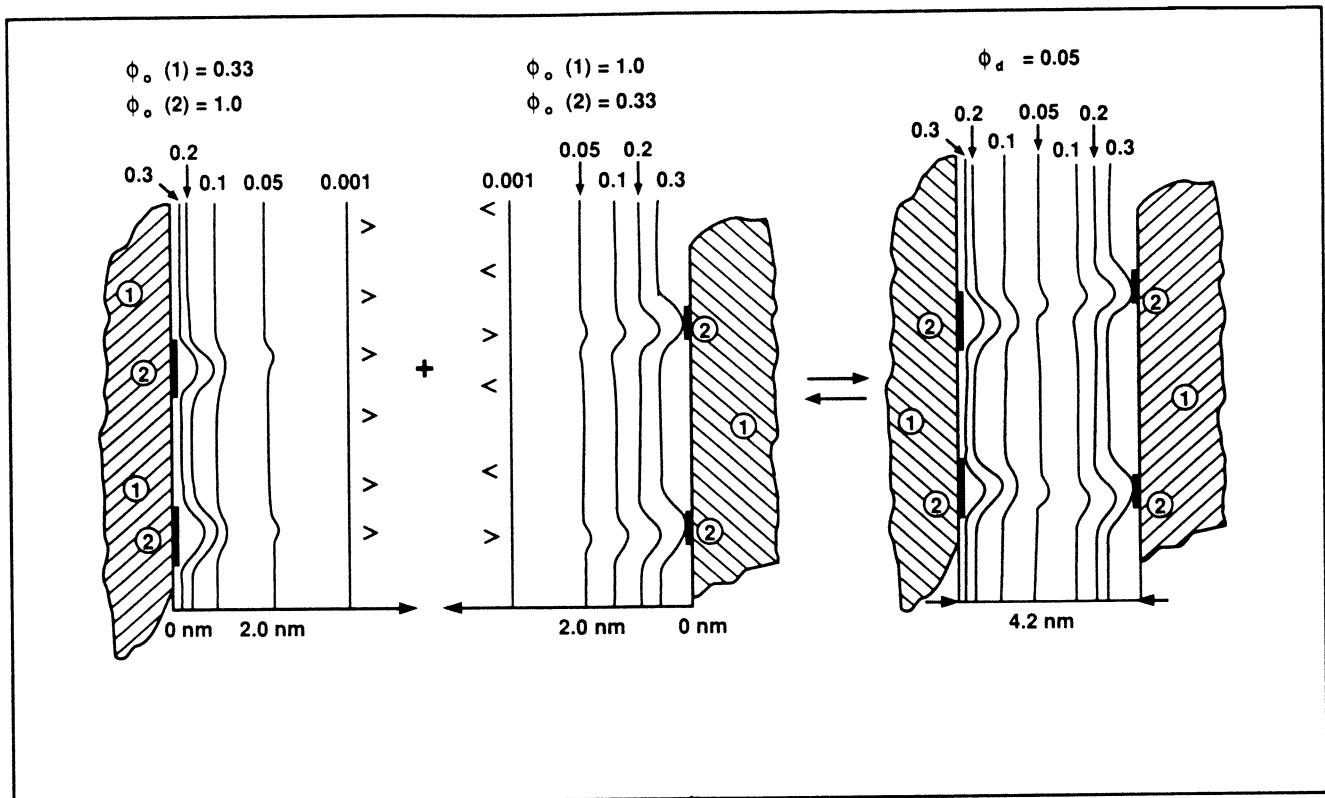
If these substances, their molecules,

or aggregates are small enough or if they have a form suited to the disintegrated system, they penetrate into the interfibrillar or interfibrous space during beating. In the pulp, at the disintegrating fiber surface, they become linked to that phase of the interface that contains suitably oriented water molecules. The orientation of these water molecules would be evoking hydration forces that attract the penetrating hydrated substances. In our terminology, this attractive hydration force results from the interaction of two hydrated phase interfaces having oppositely oriented water molecules.

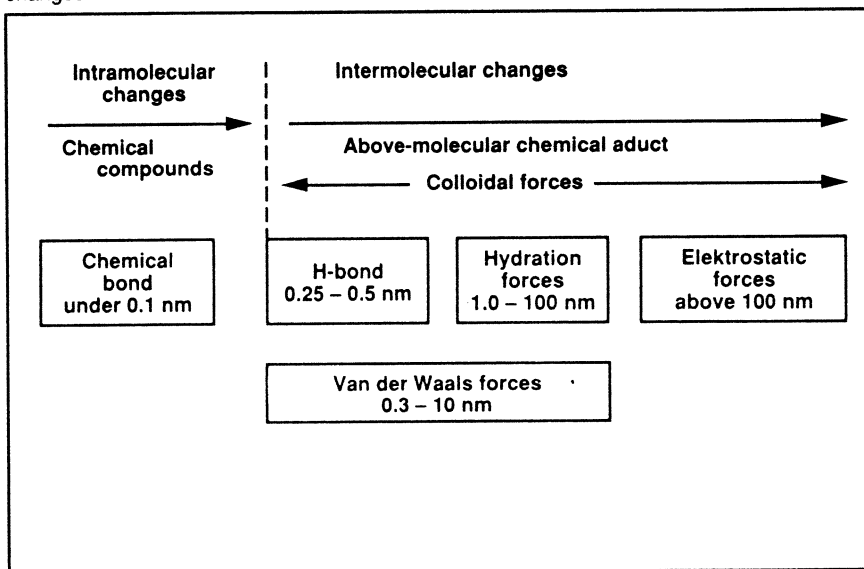
The other part of this substance—the averted part—will then give rise to repulsive hydration forces, because the orientation of water molecules on this substance is the same as that on the fiber surface to be destroyed. This repulsive hydration force is the result of the interaction of two hydrated phase interfaces having similarly oriented water molecules.

Included in Fig. 5 as an example of a substance having these effects is Congo Red. Since the 1950s (3), the application of substances showing these effects has been understood on

3. The course and dependence of isopotentials on the distance from interacting heterogeneous surfaces (attraction)



4. Distances of the actions of particular forces, defining chemical and above-molecular changes



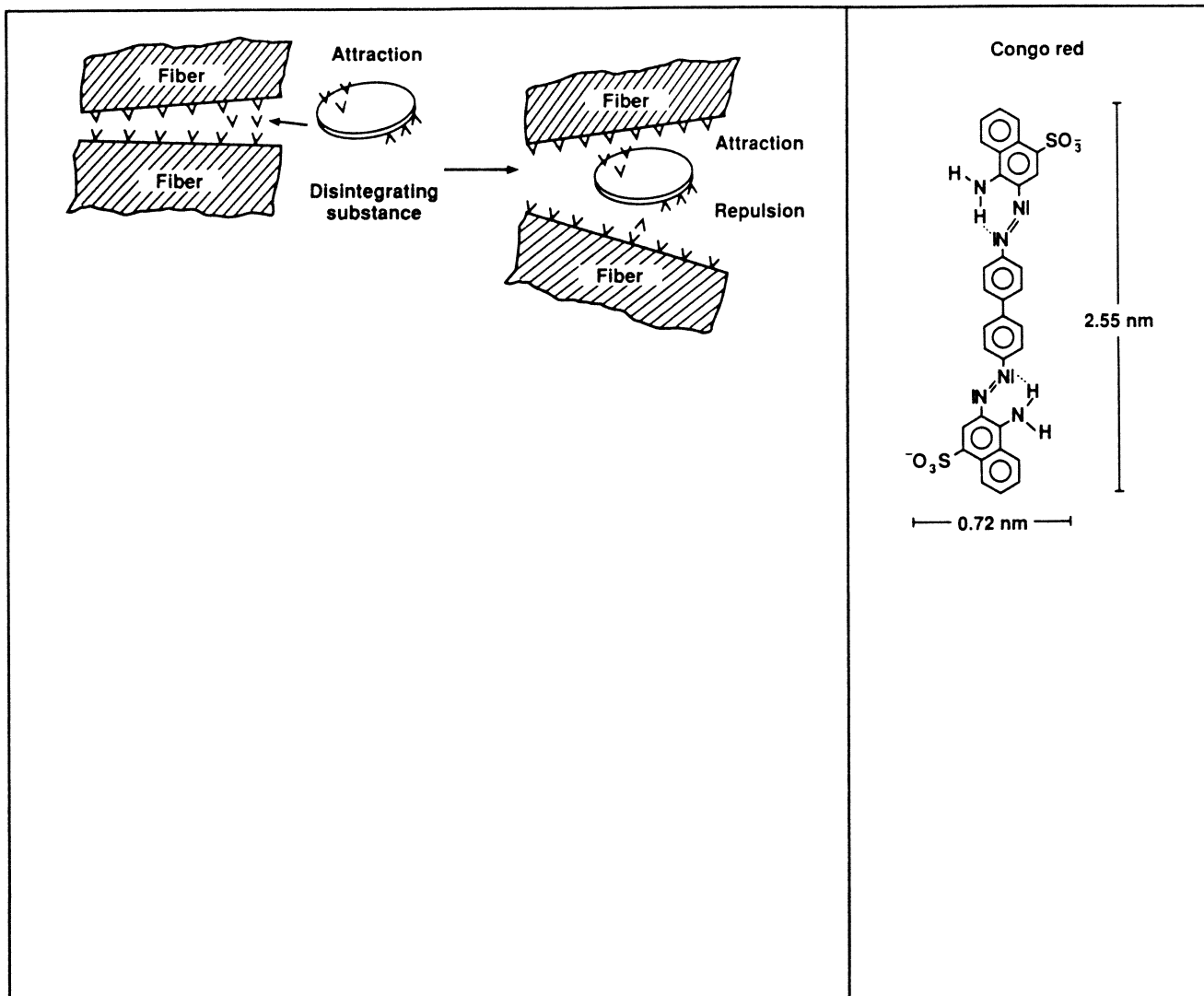
the basis of azo-dyes such as Congo Red, but their reaction mechanism has not been explained. Recently, attention has been turning again to using these substances for intensifying the beating process. Beating can be shortened by up to 55% by using Congo Red. Besides the improvement

in beating speed, strength properties are also improved in paper made of pulp beaten in this way (5). Properties similar to those of Congo Red have also been found with a range of colorless compounds, such as commercially manufactured 2,4,6-triamino-S-triazine (6).

On the basis of the SCHL theory, the capability of Congo Red and similar compounds to improve beating is determined by their convenient structure. The structure of a Congo Red molecule makes it possible for the molecule to take the linear configuration because the individual molecular fragments have a limited mobility. This mobility is more pronounced for the intramolecular H-bond of the primary amino group to the electron pair on the nitrogen adjacent to the benzidine group. This linear configuration makes it easier for the Congo Red molecule to approach closer and cling to the cellulose surface. The primary amino group is in the *trans* position to the diazo group, assuring a convenient linking and orientation of water molecules around the Congo Red molecule and its aggregates. Other beating aids are characterized by structural properties similar to those of Congo Red.

It follows from the SCHL theory that the mechanisms for phase interaction are different in the dry and wet states of fibrous pulp formations. On the other hand, the two mechanisms depend on each other. The wet action is necessary for the bonds to form in

## 5. The mechanism for substances facilitating the mechanical destruction of pulp in the beating process



the dry state, and vice versa.

### Experimental verification and practical importance of SCHL theory

The idea of the "hydration forces," from SCHL theory (11, 14), presents a new view of the chemical actions, or chemism, of the beating process and elucidates the mechanism through which beating aids act. Although the processes mentioned seem relatively simple at first sight, a closer look changes the matter. The extent to which hydration forces are of use depends upon:

- The heterogeneity of interacting surfaces, defined by the fact that qualitatively different types of

groups are contained in each surface unit, accepting water molecules of different orientation by means of H-bonds

- The quality or size and type of H-bonds between individual groups and water molecules at the phase interface
- The quantity of qualitatively equal groups in a unit of interacting surfaces, with these groups accepting water molecules by means of H-bonds.

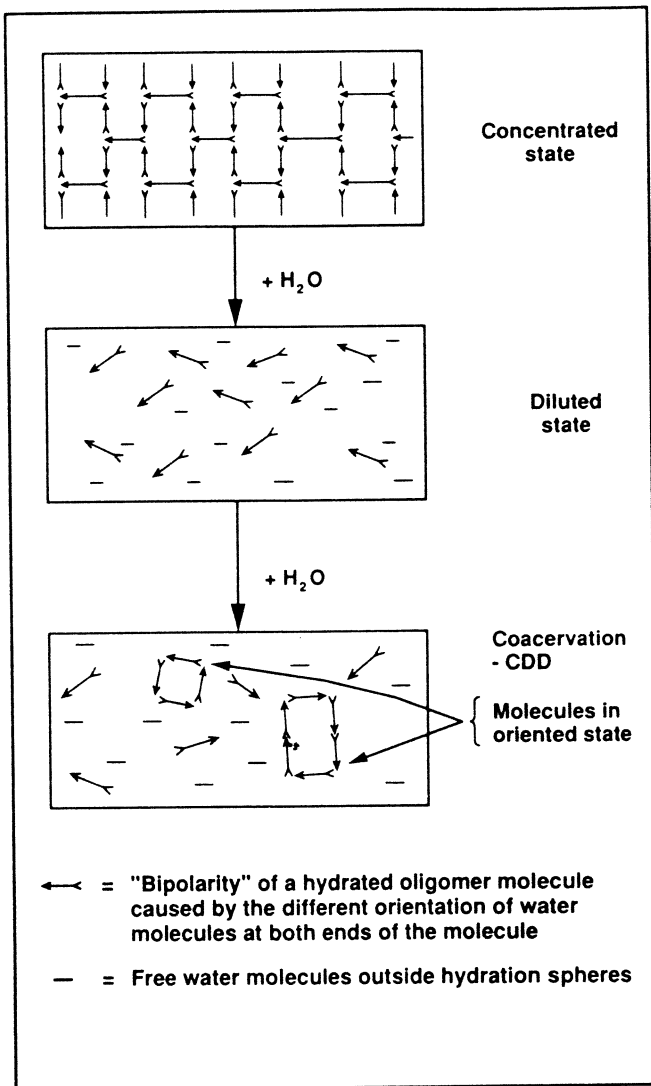
Although there are only two basic orientations of water molecules with respect to the interacting phase interfaces, the problems are complicated. The chemical structure of pulp is considerably heterogeneous, and the factors that influence the action of

hydration forces have various effects. To learn the chemism of beating processes, we have to find simulations to better evaluate the hydration forces applied and to learn how to influence them. Characterizing these quantitatively would be then an ideal aim.

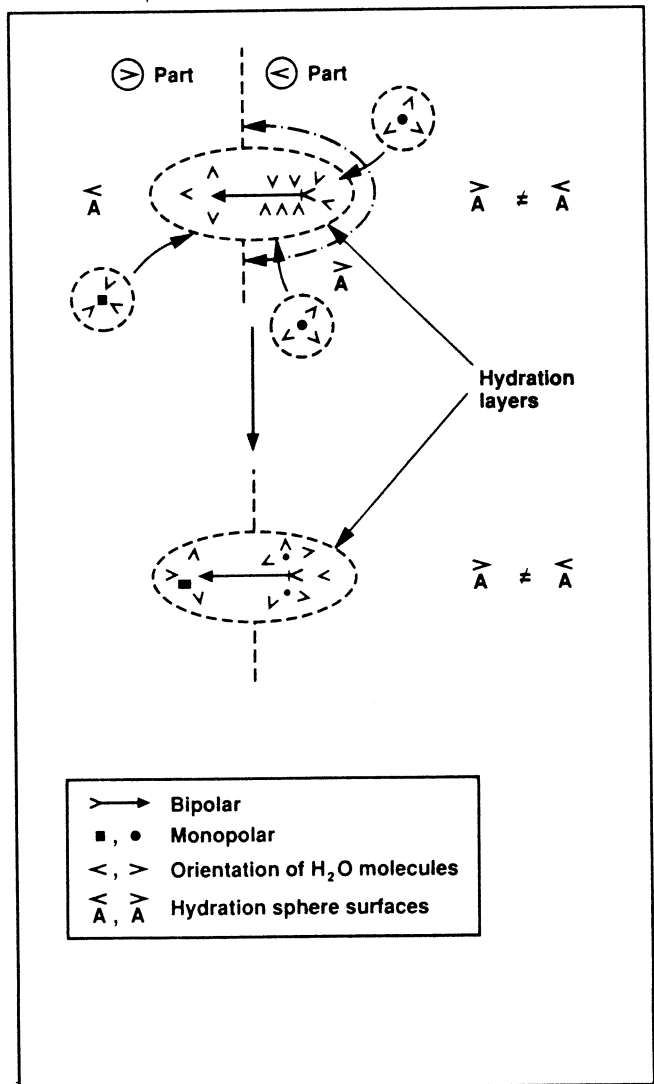
### Evaluation of the effect of hydration forces

If these hypotheses are correct and are of practical importance, they must have common validity. This means there must exist some systems other than cellulose or polysaccharide ones in which similar phenomena connected with the hydration forces are of use. These are hydrated hydrophilic systems (9, 14) characterized with a so-called "critical degree of dilution" (CDD) that may simulate the action

6. The behavior mechanism of the bipolar, hydrated, oligomer system on being diluted with water beyond the critical degree of dilution



7. The mechanism by which the orientation of water molecules changes in hydration spheres around the oligomer hydrophilic molecules of bipolar nature when other compounds are added.



II. Influence of several auxiliary substances on the hydration forces in a simulated system formed by urea-formaldehyde precondensate

Substance	<i>f</i>	Increase of hydration forces	Dosage, %
Congo Red	0.70	Repulsive	1.0
K <sub>2</sub> SO <sub>4</sub>	-0.11	Attractive	3.0
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·	-0.15	Attractive	6.0
Process water	-0.11	Attractive	...
NaCl	0.07	Repulsive	3.0
Acetamide	0.6	Repulsive	20.0
Na polystyrene maleinate	-0.24	Attractive	1.0
Na polystyrene maleinate	0.29	Repulsive	10.0
2,4,6-triamino-S-triazine	0.025	Repulsive	0.5
Distilled water	0.0	...	...

of these hydration forces. This behavior is typical for some hydrophilic substances of oligomer nature, such as several precondensates and polyesters, that form optically homogeneous systems in a concentrated state with water. When gradually diluted after having reached the CDD, the oligomeric solution gets turbid, which is caused by coacervation of individual hydrated, hydrophilic molecules resulting from the attracting action of hydration forces.

If  $V_0$  is the initial volume of the hydrated hydrophilic solution and  $V$  is the dilution volume added that induced turbidity, then

$$CDD = V/V_0 \quad (1)$$

The behavior of such systems can be

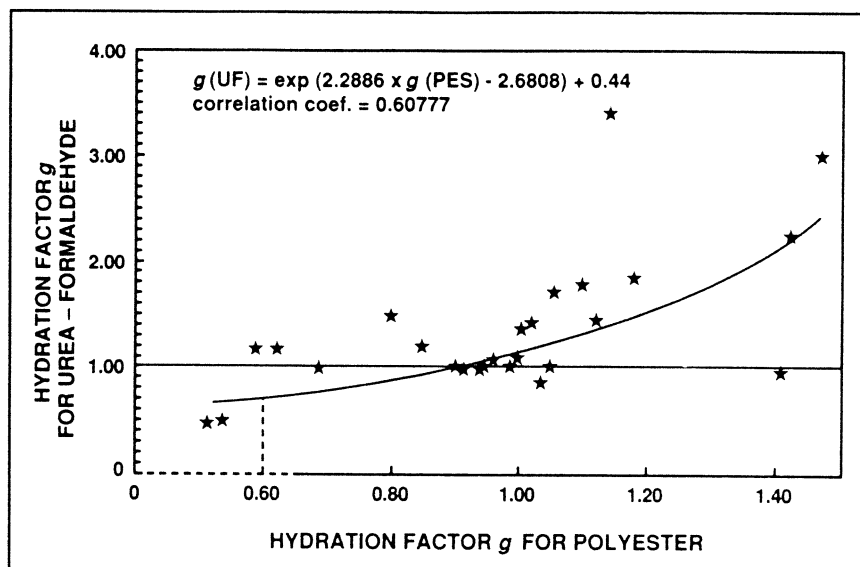
simply explained by the hydration forces concept. Figure 6 represents the behavior mechanism of these systems. For such behavior to take place, hydrated, hydrophilic, nonisometric, oligomer molecules of a relatively rigid nature have to be in water. As Fig. 7 shows, both ends of the nonisometric hydration sphere are formed by water molecules with opposite orientation. The whole hydrated molecule thus appears to be bipolar in considering it from the view of the hydration forces effect. The distribution of localities with equally oriented water molecules does not have to be symmetrical.

From Fig. 7, we can see that hydrated molecules of other additives are drawn to the appropriate localities of the hydrated oligomer molecule by hydration forces that attract, changing the distribution of water molecule orientation in these localities. Accordingly, depending on the composition of oligomer molecules, the localities with < orientation of water molecules can predominate around some molecules, and localities with > orientation can predominate around others. Certain behavior differences can thus occur in such systems, especially on using other additives to influence their behavior (Table II).

As represented in Fig. 6, individual oligomeric molecules are evenly distributed in the whole water area at concentrated state (at room temperature, when hydration forces are functioning to a sufficient extent). Minimum internal energy can be reached, with all water molecules contained only in mutually diffusing hydration spheres around the oligomeric molecules. The whole system is isotropic with regard to the sizes of its structural units and is more viscous owing to the attraction of hydration forces. (The lower the CDD, the higher the viscosity.) In the system, hydration forces that repulse alternate regularly with hydration forces that attract.

On gradual dilution, hydrated oligomeric molecules separate from each other, becoming more free and mobile owing to the uneven effect of attractive and repulsive forces and to the convective motion of heat. They are less and less limited in their motion, so that they take a more preferable orientation in their collisions. Owing to their nonisometric form, some molecules take a new,

8. Relationship between the hydration factors of hydrated hydrophilic systems characterized with CDD



better arranged state at a suitable moment, becoming oriented to each other in a certain order similar to the initial concentrated state. Coacervation takes place, in which the properties of individual coacervated particles resemble the initial highly concentrated system of the hydrated hydrophilic oligomer compound.

The CDD value thus characterizes, even if indirectly, the extent to which hydration forces are at work. The addition of substances that interfere with attracting hydration forces increases the CDD value, and the addition of substances that interfere with repulsing hydration forces decreases the CDD value.

It is preferable to evaluate the relative effect of these additives in relation to distilled water, by means of hydration factors  $f$  and  $g$ , which are defined mathematically. If  $CDD_0$  is the critical degree of dilution in distilled water and  $CDD$  is the critical degree of dilution with the addition of the examined substance, then the relation is:

$$f = (CDD - CDD_0) / CDD_0 = g - 1 \quad (2)$$

where

$$g = CDD / CDD_0.$$

A positive  $f$  value ( $g > 1$ ) indicates a decrease of attracting hydration forces or an increase of repulsing forces—a positive effect of the added

substance in the beating process. On the other hand, a negative  $f$  value ( $g < 1$ ) indicates a decrease of repulsing forces or an increase of attracting forces.

Figure 2 shows the relation of hydration factors determined by means of two qualitatively different hydrophilic systems—(a) urea-formaldehyde precondensate with (b) oligomeric polyester. Recall that hydration factors change with the amount and type of chemical aids added. The data in Fig. 2 were obtained mainly with the use of various chemicals. The mutual relationship of the hydration factors of urea-formaldehyde precondensate (UF) with polyester (PES) can be described by the following equations, where  $r$  is the coefficient of correlation:

$$g_{UF} = 1.381 g_{PES} - 0.026 \quad (3)$$

with

$$r_{xy} = 0.5383$$

or

$$g_{UF} = \exp(2.29 g_{PES} - 2.68) + 0.44 \quad (4)$$

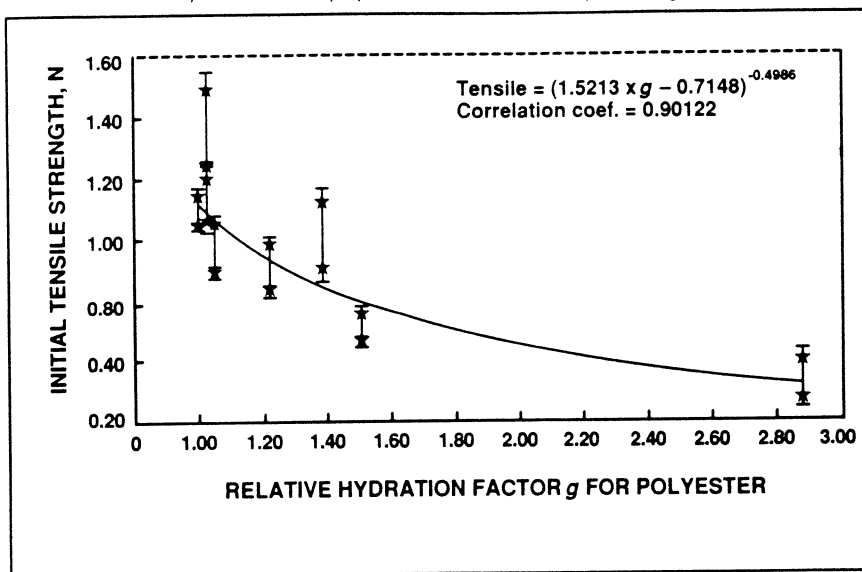
with

$$r_{xy} = 0.6078$$

In accordance with these equations, the only mutual relationship between these hydration factors is a qualitative one. The experimental data are con-



9. In this plot against initial tensile strength, the relative hydration factor  $g$  was measured over a range extending from water from pulp slurries without other components ( $g = 1.00$ , where  $CCD = CCD_r$ ) to water from pulp slurries with other components ( $g > 1.00$ ).



siderably dispersed, but this variance is not caused by a poor reproducibility in the method. Instead, it is caused by qualitative differences in the behavior of both systems with regard to the nature of hydration forces at work. This difference can be explained theoretically by the concepts illustrated in Fig. 7. For instance, the  $<$  orientation of water molecules around interacting oligomer molecules prevails in the first system, whereas the  $>$  orientation prevails in the second.

Besides the additives that aid the beating process ( $f > 0$  and  $g < 1$ ), there are also substances that have the opposite effect, as we see from Fig. 8 and Table II. The nature of this effect may even vary with the dosed amount (with, for example, sodium polystyrene maleinate). Furthermore, real process water contains various substances that can affect the hydration forces action both in positive and in negative ways. For instance, we can see from Table II that the presence of sulfate anions has a negative influence on repulsing hydration forces and, consequently, on the beating process. At the same time, the presence of sulfate anions in recycling white water has been quite common until now. As a result of these sulfate anions, the beating process requires more energy and may take more time.

#### Semi-quantitative proof for the existence of hydration forces

A direct proof of hydration forces has not been given until now. However, observations have been made that can be explained in some cases only by means of SCHL theory and the existence of hydration forces (16).

The strength of the bonding system of the wet paper web is defined by the mechanical entanglement of the fibers and the mutual physical bonds between them. The extent of the ability of fibers to bond increases with the increase in the degree of beating. If a constant contribution to mechanical entanglement is assured in the bonding system of the wet paper web, such as with a constant degree of beating, then the changes in the initial tensile strength of the wet paper web will indicate the changes in interfiber bonds. When these mutual bonds result from hydration forces, the initial strength will directly indicate their changes, and the final strength of the web will depend on them.

If we accept this theoretical concept for the mutual force effect of interacting hydrophilic pulp fibers of medium and high consistency ( $> 12\%$ ), such results can be taken for a semi-quantitative proof of the existence of hydration forces.

This theory is verified in Fig. 9, with the relationship of the initial tensile strength of paper to the rela-

tive hydration factor

$$g = CDD_r / CDD_r \quad (5)$$

where  $CDD_r$  is the critical degree of dilution in paper stock water without other aids. In the figure, the experimental dependences found can be described with the linear relationship described by Eq. 6:

$$Tensile_{initial} = 1.4 - 0.32 g \quad (6)$$

with

$$r_{xy} = -0.754$$

Alternatively, we may use the non-linear relationship of Eq. 7, which better agrees with the dependence:

$$Tensile_{initial} = 1 / (1.52 g - 0.715)^{0.5} \quad (7)$$

with

$$r_{xy} = -0.901$$

The dispersion variance of experimental values around the counted relation was caused, in this case, by a lower reproducibility in determining initial strength.

#### The influence of hydrated hydrophilic substances onto the beating process

By simulating hydrated, hydrophilic systems, we have a chance to examine the influences of the medium and of various beating aids on hydration forces and thus on the beating process. Substances that increase the hydration factor  $f$  above the value of zero—that is,  $g > 1$  with distilled water—will then decrease the effect of attracting hydration forces and thus the beating energy and the initial strength of the paper web. Figures 9 and 10 show the relationships of the relative hydration factor to the initial tensile strength and the beating energy consumed, both of which serve as evidence.

The relationship of the beating energy consumption  $C$  to the relative hydration factor  $g$ , given in Fig. 10, can be described with Eq. 8:

$$C, \% = 260.1 - 178.2 g \quad (8)$$

with

$$r_{xy} = -0.5067$$

Preferably, a nonlinear relation could be used:

$$C, \% = (26.75 - 14.87g)^{1.77} \quad (9)$$

with

$$r_{xy} = -0.6072$$

A considerable dispersion variance of the values around the counted relationship is caused not only by a fault in measuring the beating energy consumption and factors that can influence it (such as pulp consistency). It is caused, first of all, by possible differences in the distribution of hydration forces in the pulp and in the simulated system of urea-formaldehyde precondensate.

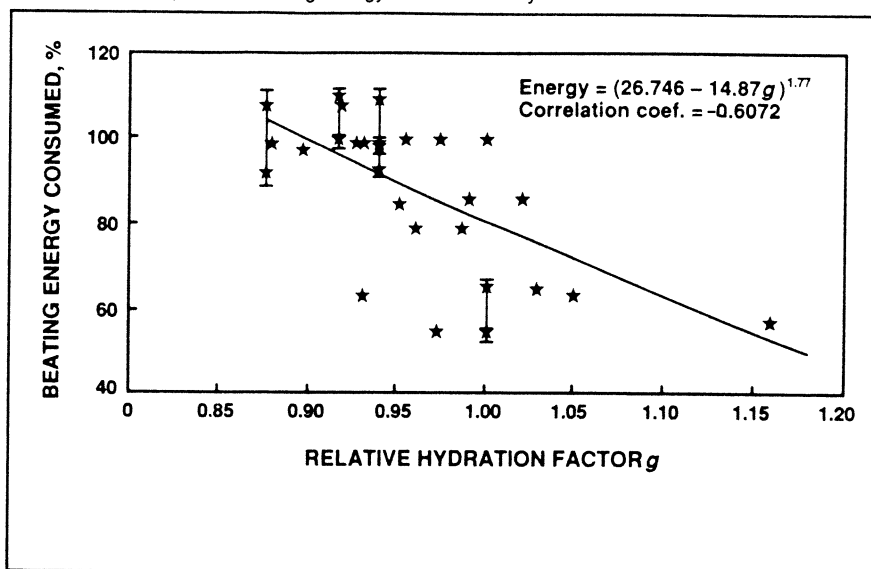
The decrease in relative energy for pulp beating varies with the degree of beating. **Figure 11** shows typical plots for this relationship. The relative decrease in beating energy requirements increases with freeness, but it increases to a lesser extent in the range of 25–55°SR. At higher freeness—i.e., above 60°SR—the relative decrease of beating energy is greater. For this reason, the data on beating energy consumption are related to the universal beating degree of 50°SR.

The consumption of energy needed for beating pulp to 50°SR (Schopper Riegler freeness) with respect to the beating energy in fresh water can be estimated from the relationship in Fig. 10 or from Eqs. 8 and 9. Notice that the value of  $g$  at 100% of the beating energy consumed does not equal 1.0 but about 0.9. This means that the synergistic effect of the soluble substances released from pulp and other additives in the course of beating has a positive influence on beating energy requirements.

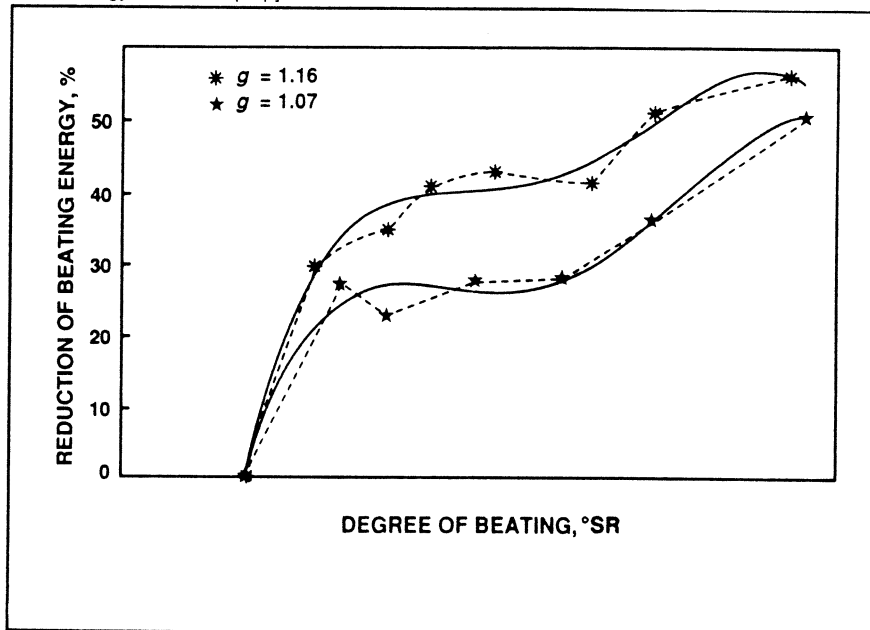
The results from simulated examinations were verified with beating experiments in the laboratory, in a pilot plant, and on the commercial process scale. At first, it was to establish whether the behavior found with the simulated system does agree with actual beating behavior, at least from the qualitative side. Based on long-termed observations, we can say that there was not a single case tested in the simulated system, such as increasing the effect of repulsing hydration forces, that would behave in another manner in beating.

The quantitative relationship between the simulated and beating experiment can be seen in Fig. 10 and is described with Eqs. 8 and 9. This enables us to evaluate and control the beating process in plants for its

10. The consumption of beating energy  $C$  on relative hydration factor



11. The reduction of beating energy with beating aids on degree of beating (°SR). The percent reduction of beating energy =  $100 \times [(\text{energy for pulp with beating aids} - \text{energy for control pulp}) / \text{energy for control pulp}]$



energy requirements in accordance with actual operating conditions.

The analysis shows that the effect of direct beating aids is highly dependent on the composition of process water. It may happen that, while good results are reached with the use of a particular beating aid in one paper mill, the results could be substantially less satisfactory in another. The composition of process water is defined by various aspects—starting with the fresh water composition, its recirculation together with the dosage

of chemical aids to the system, and, last but not least, the cleanliness of introduced raw materials, mainly of pulp. The badly washed pulps and alum dosage usually deteriorate the beating process.

## Conclusions

On the basis of described common theoretical conceptions, a simulated system can be prepared to serve as a simple tool for evaluating the action of beating aids and the influence of a water

medium on beating. This makes possible a more qualified intervention in the beating process and its intensification.

By making use of the action of hydration forces and influencing them, some improvements may be brought about in smooth running at the wet end of paper machines and in other defibrillation and refining processes, such as those connected with chemical treatment. This ability should be of further importance for intensifying the production of high-yield mechanical pulps.

### Experimental procedures

The hydration factor  $f$  or  $g$  was determined by means of simulated systems with urea-formaldehyde precondensate and polyester on the basis of maleic anhydride, glycerol, and ethylene glycol. With distilled water at 20°C, the  $CDD_0$  values were 3.0 for urea-formaldehyde and 3.6 for polyester.

The CDD values were determined turbidimetrically on a common spectrophotometer. Dilution water was gradually added to the urea-formaldehyde precondensate or polyester system contained in a cell fitted with a magnetic stirrer. When the CDD is reached, there is a strong drop in the light radiation transmittance ( $\lambda = 850$  nm).

The hydration factor values found with the urea-formaldehyde precondensate gave a better possibility of correlating with the results of beating experiments. Therefore, we determined the  $g$  or  $f$  values mainly by means of this simulated system.

The initial tensile strength of wet paper web was determined with the Brecht-Heiniger method (23) and apparatus. Bleached softwood sulfite pulp beaten to 48°SR (Schopper-Riegler) was used for the experiments. The results for initial strength were then converted to uniform 15% dry matter and a basis weight of 100 g/m<sup>2</sup> (24). Experimental error was about 10%.

The results of beating experiments described in Figs. 10 and 11 were obtained by beating bleached softwood sulfate and sulfite pulps on a pilot disc refiner usually at 3% consistency. Energy requirements were measured in a common electrical way. The transport of pulp suspension through the refiner was provided with a separate slurry pump whose electric input was separately measured. Beat-

ing degree was determined according to the Schopper-Riegler method.

The influence of consistency within the range of 1.5–3.5% on the relative beating energy requirements was statistically insignificant under the given conditions. Fresh water from water works was used as the basic medium for comparative purposes. Beating energy consumption in this medium without any chemical aids was 100% (control experiment). □

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### Appendix: the main types of H-bonds possible forming the above-molecular structure of cellulose

#### Intramolecular H bonds

These include:

- C'(2)OH-C(6)OH
- C'(3)OH-O(ring)

#### Intermolecular H bonds

H-bonds linking up single cellulose chains in the planes located one above the other:

- C'(2)OH-O(ring)
- C'(3)OH-O(ring)
- C'(6)OH-O(ring)
- C'(2)OH-C(3)OH
- C'(6)OH-C(2)OH
- C'(6) OH-C(6)OH
- C'(6)OH-O(linking)

H-bonds linking single cellulose chains located in the same plane:

- C'(6)OH-C(6)OH
- C'(6)OH-C(2)OH
- C'(6)OH-O(ring)

#### Strength order of particular H-bonds

The strength order is:

intra C'(6)OH-C(2)OH >

intra C'(3)OH-O(ring) =

inter C'(6)OH-C(2)OH =

intra C'(6) OH-C(6)OH =

**Appendix, contd.**

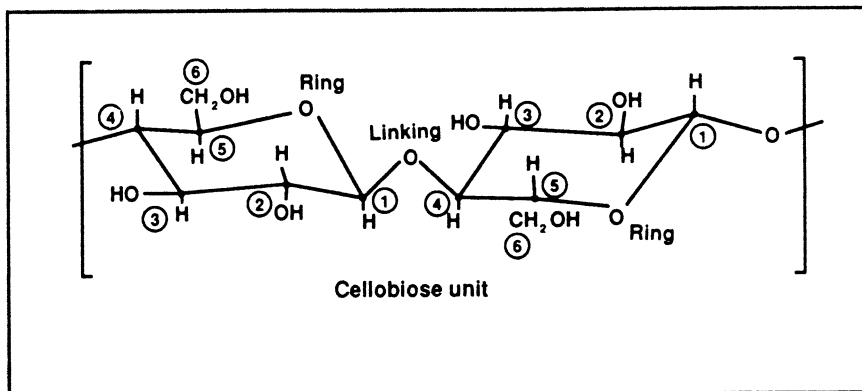
intra C'(2)OH-O(ring)=

intra C'(6)OH-O(linking)&gt;

intra C'(6)OH-C(2)OH in the  
plane>

intra C'(3)OH-O(ring)&gt;

intra C'(2)OH-C(3)OH



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