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THE ROLE OF PULP FRACTIONS AND PROCESSING VARIABLES IN RECYCLING

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THE use of recycled pulps in the paper industry is increasing in importance. This is a result, not only of the growing deficit of fibrous raw materials in many regions of the world, but also of the mounting concern to protect the environment from the effects of waste paper garbage and its products of combustion.

Not long ago, the use of recycled waste paper for papermaking was limited by the organisation for collection and sorting; the technical problems associated with new slushers, defibrators, sorters, cleaners and thickeners; the technological problems of contamination from plastics and metal foils; the difficulties in dispersing fusible waxes and bituminous substances and in the deinking of secondary pulp made from printed papers.

However, in many cases, progress with these problems is not in itself sufficient to enable increased use of waste paper in the production of a wide range of paper products.

The main difficulty now is that of providing the necessary mechanical properties in the paper containing secondary pulps without, at the same time, giving rise to drainage problems on the paper machine. This problem is of significant economic importance and many respected research centres in Europe and the U.S.A. are now paying attention to it.

Fundamental investigations have been done in the research centres at Appleton,(1) Stockholm,(2–5) Manchester,(6, 7) Darmstadt,(8, 9) Madison,(10, 11) Helsinki,(12–13) and Łódź(14–19) as well as in other laboratories.

Investigations have been made to establish the effects of multiple recycling upon the characteristics of paper pulps and the papers made from them. Subjects for study have included: the influence of pulp type and method of pulping; the influence of the number of cycles and the loss of fines; the influence of beating in various ways; the influence of various methods of drying.

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In each case these factors have been related to the properties of the resulting stocks and the papers made from them.

As long as 30 years ago Brecht(20) observed that (for the same refining time) the original pulp has a lower wetness, lower density and greater absorbency than does the same material when recycled. Most important of all, recycling reduces strength.

During the past 7 years various research workers have simulated the multiple recycling of pulps. They have used defibring cycles with no beating, beating to constant paper density or breaking length or, sometimes, to constant pulp wetness. All have reported considerable changes in the properties of the recycled pulp, attributing them mainly to irreversible changes in the structure of dried fibres.

These fibres have a reduced ability to form bonds, an increased susceptibility to wetness from beating and a decreased swelling capability. Even partial recovery of the swelling ability by beating leads to excessively poor drainage on the machine.

Following these investigations, some suggestions have been made for methods which could allow improved mechanical properties of papers from secondary pulp without the usual drainage problems. These ideas include slushing in an alkaline medium or mild refining or beating at high consistency. The large research programmes are now leading to explanations for the fundamental changes which occur during recycling.

It appears to be essential to establish the relative importance of the fibrous and fines components of the pulp in the observed changes. This matter has been the subject of extensive studies made at the Institute of Paper making and Paper Machines of the Technical University in Łódź.

Three sets of experiments were carried out in an attempt to establish the influence of the two pulp fractions upon the now well known phenomena occurring during the making of secondary pulp into paper.

In the first set of experiments an unbleached sulphate pulp, beaten to 43°SR, was subjected to 3 cycles. Each cycle consisted of defibring (without beating) forming and drying. The recycled pulp showed a gradual decrease of wetness and breaking length. The effect was the most marked after the first cycle and less for successive cycles.

Analysis of the water retention value of recycled pulp and of its fibrous fraction (Fig. 1) indicates that the decrease in this index is due to the increase of fibre swelling capacity.

From these data and the changes in the fines fraction in the recycled pulp, it was calculated that the WRV of this fraction was decreased by recycling from *ca.* 600 per cent to *ca.* 400 per cent. This means that this fraction be-

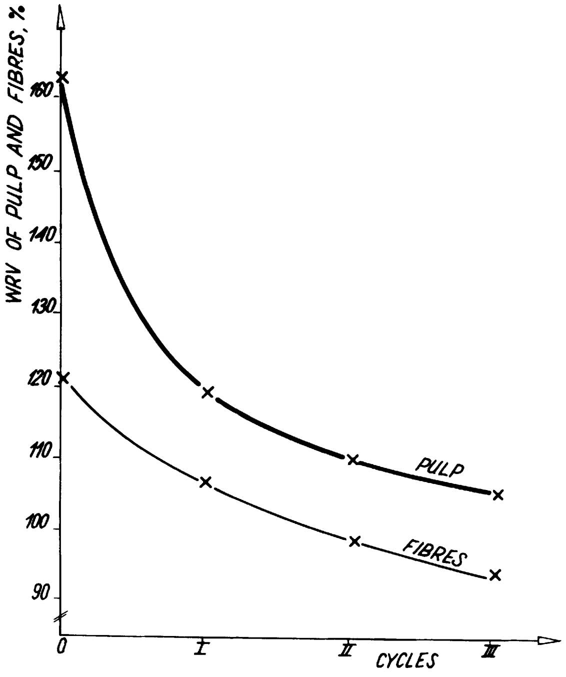

Fig. 1—Effect of Recycling (formation, drying and defibring) on water retention value of kraft pulp and of its fibrous fraction

comes hornified, thus causing a loss of swelling capacity of the recycled pulp.

Our previous work showed that there was a close relationship between the WRV of fibres and the breaking length of paper made from them (Fig. 2). We also reported that fines from recycled pulp increased the breaking length of paper to a lesser degree than did the same quantity of fines from beaten virgin pulp. This could be expected from the higher WRV of the fines in virgin pulp.

From these facts we may conclude that the worsening of the mechanical properties of recycled pulp is due to the fact that, not only the fibres, but also the fines of recycled pulp become hornified.

The second set of experiments was carried out in order to explain how the unwanted hornification effects, seen in recycled pulps, may be diminished by beating. In these experiments the pulp was beaten up to the point where maximum breaking length was achieved for each cycle.

Recycled in this way, the pulp did not show a decreasing wetness, but, in

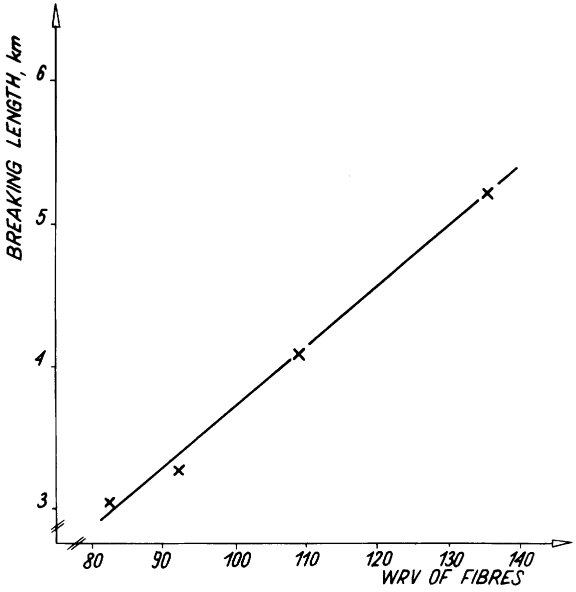

Fig. 2—Relation between WRV of fibres and breaking length of paper obtained from the fibrous fraction

contrast, to the first set of experiments, a sharp increase in wetness was observed. The fibrous fractions showed only a small increase in wetness (Fig. 3).

The observed large increase in pulp wetness is therefore associated with the fines content, which increases almost five-fold due to recycling (Fig. 4) despite some slight losses during the subsequent sheet forming processes.

The swelling capacity of pulp, as well as of its fibrous fraction, decreases more slowly than in the first set of experiments; the decrease, totalling some 17 per cent, compared with 30–36 per cent when recycled without beating. Fig. 5 shows that the effect was associated with a considerable decrease in WRV of the fines fraction.

On the other hand, the specific surface area of the recycled pulp and of both its components increases in each cycle (Fig. 6). This effect is clearly derived from the beating because, when recycled without beating, the specific surface area of pulp decreases (Fig. 9).

As a result of these changes, and also of the shortening of the fibres, a gradual decrease in breaking length of paper from the recycled pulp was observed (Fig. 7). In the second set of experiments (with beating) the effect was only about 15 per cent compared with the decrease of about 60 per cent

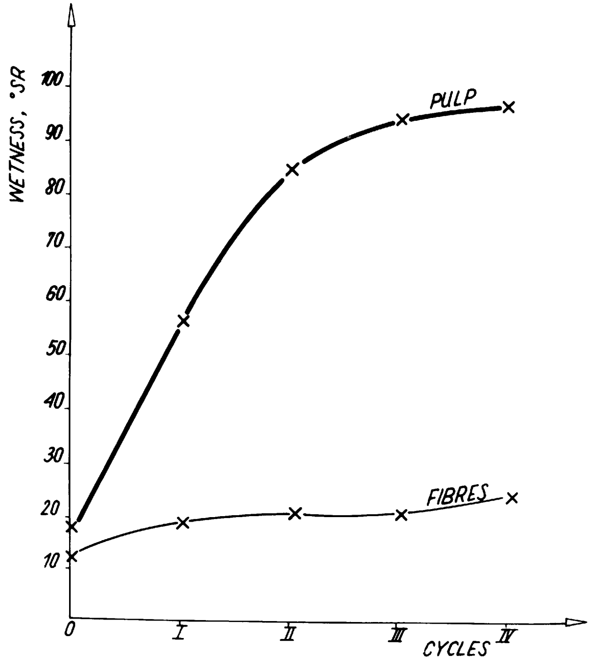

Fig. 3—Effect of recycling (formation, drying, defibring and refining) on wetness of the bleached pine sulphate pulp and of fibrous fraction

seen in the first set (without beating). The decrease in breaking length associated with the fibrous fraction alone was even smaller at about 8 per cent. These results indicate that the fractional components of the pulp do not react identically during recycling with or without beating.

Recycled fibres become hornified without beating, as illustrated by a decrease in WRV, whilst at the same time their wetness, specific surface area and associated breaking length also tend to decrease.

In contrast, when pulp is beaten to maximum breaking length at each cycle. the phenomenon of hornified fibres is almost completely suppressed. This can be deduced from the relatively small decrease in their WRV and associated breaking length with a simultaneous increase in specific surface area, wetness and susceptibility to beating. In each successive cycle the fines become more completely separated and the WRV, specific surface area and associated breaking length increases more and more quickly.

Recycling without beating also causes hornification of the fines with

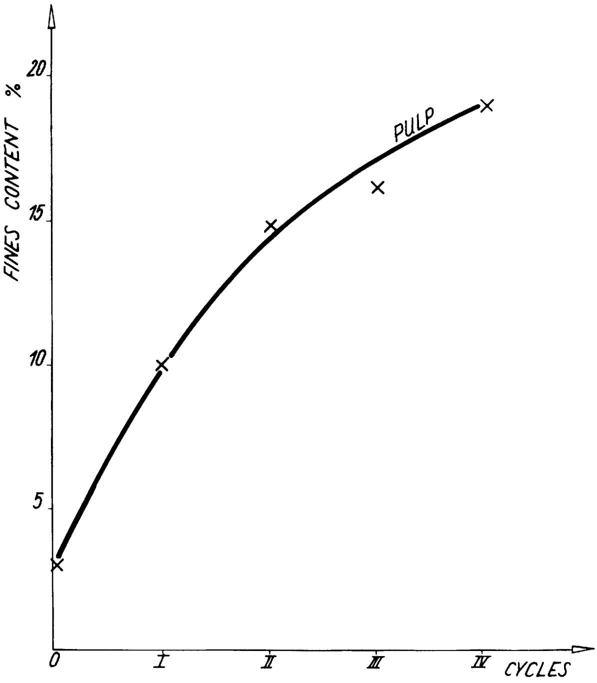

Fig. 4—Effect of recycling (formation, drying, defibring and refining) on fines content in the bleached pine sulphate pulp

considerably reduced WRV. However, unlike for fibres, recycling with beating does not suppress the effect (as measured by reduction in WRV of the fines). In fact a considerable increase in the specific surface area of this fraction may be observed. This suggests continuing disintegration; thus causing a serious increase in wetness without improving the ability of the fines to assist fibre bonding.

For these reasons it is proposed that the well-known phenomenon of hornification of pulp from recycled waste or dry broke is due in large part of the fines fraction. The fines considerably increase the wetness of recycled, beaten pulp, but are not so effective in improving the associated breaking length.

The consideration of irreversible hornification of recycled pulps can explain the influence of consecutive production processes on paper and board, from which the recycled pulp was obtained, upon the papermaking capabilities of these pulps. In particular, there is an explanation of the effects of beating

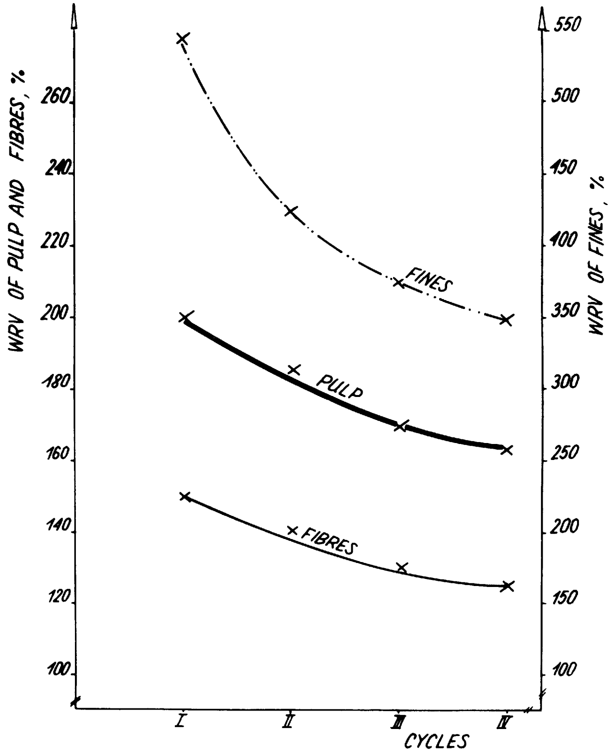

Fig. 5—Effect of recycling (formation, drying, defibring and refining) on water retention value of bleached sulphate pulp and of its fibrous fraction and fines

virgin pulps (and making dry paper from them) upon the changes in basic fractional components of the subsequent recycled pulp.

Arising from these ideas, a third set of experiments was carried out.

Three experimental pulps were prepared:

Virgin pulp (PO)	Bleached pine sulphate, never-dried and at 30 per cent moisture content.
Recycled pulp (P1)	Pulp PO after forming and drying on a laboratory papermaking machine.
Recycled pulp (P2)	Pulp PO after beating in a Valley beater to 50° SR and formed and dried on a laboratory papermaking machine.

These pulps were beaten for times between 0 and 60 minutes in a Valley

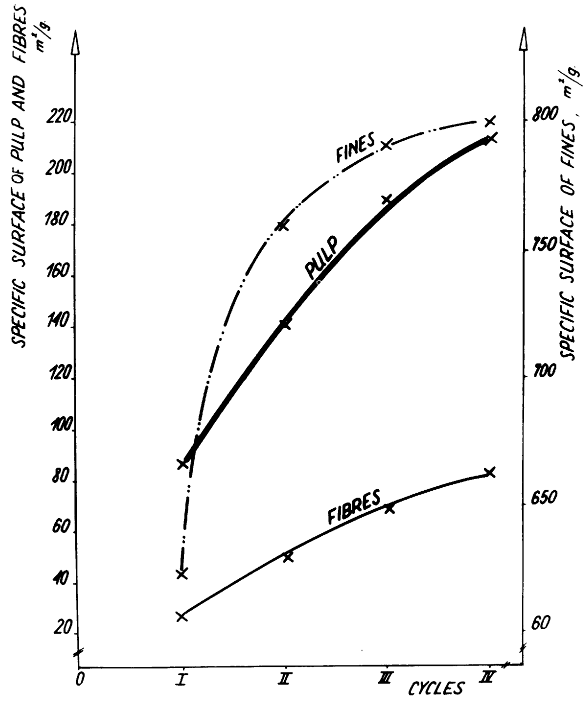

Fig. 6—Effect of recycling (formation, drying, defibring and refining) on specific surface of the bleached pine sulphate pulp and of its fibrous fraction and fines

beater. Every 15 minutes samples were collected, sheets were made on a Rapid Köthen apparatus and their properties measured.

The results were analysed to determine the effect of the beating, forming and drying processes and also the effect of changes in the quality and quantity of the pulp fractions upon:

(1) The properties of the recycled pulps.
(2) The properties of the paper made from these pulps.
(3) The effective papermaking capabilities of recycled pulps.

The WRV is one of the most important indicators characterising papermaking ability. Study of WRV results from this third set of experiments (Fig. 8) shows that the decrease in WRV of the experimental recycled pulp, compared with the virgin pulp, is mainly due to the negative influence of the forming and drying processes in which the fibrous fraction is dominant.

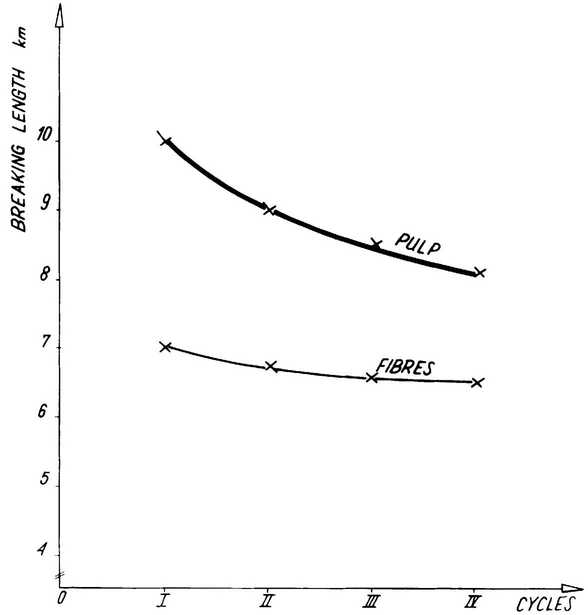

Fig. 7—Effect of recycling (formation, drying, defibring and refining) on breaking length of bleached pine sulphate pulp and of its fibrous fraction

There is also a weaker, but positive, influence due to beating the virgin pulp where the principal effect is due to the fines.

Pulp P1 (from formed and dried virgin Pulp) had less fines than did the virgin pulp. On the other hand, pulp P2 (from formed and dried virgin pulp after beating) had more fines than did virgin pulp (Fig. 9). The wetness of these experimental pulps is in line with this. Any increases in wetness are due mainly to the beating of the virgin pulp (Fig. 10), offset slightly by the forming and drying processes. In both cases the effect of the fines fraction is dominant.

Turning now to the properties of the papers made from the experimental pulps, it is clear that the forming and drying processes cause most of the decrease in breaking length, with the beating of the virgin pulp contributing to a lesser degree (Fig. 11). The main culprit for decrease of breaking length is the fibrous fraction, whereas the fines mostly cause a slight increase. The effects upon burst figure were similar.

Tearing strength analysis (Fig. 12) indicates that the decrease of tearing strength for paper made from experimental recycled pulp is caused definitely by beating the virgin pulp, whilst improving this strength characteristic. It is

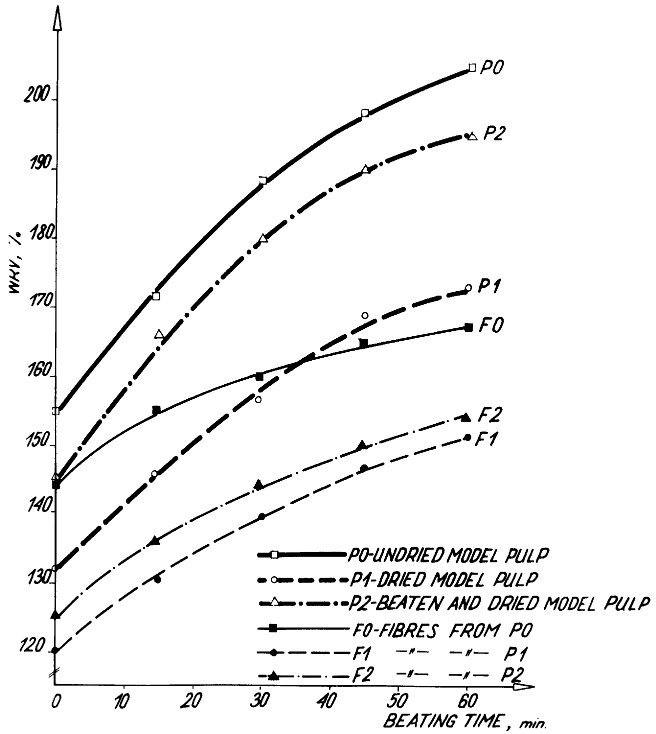

Fig. 8—Effect of beating model pulps on the water retention value of these pulps and of their fibrous fractions

interesting that, in this case, both fibrous fraction and fines have practically identical shares in these changes.

A useful index of a paper's general strength is the relationship between tearing strength and breaking length in the sense that the outer curves in a graph, such as Fig. 13, where one is plotted against the other, are associated with papers suitable for uses where good mechanical properties are required. Roughly speaking, the index we are concerned with is the product of tensile and tear strengths. Changes in this index for the experimental pulps and their fibre fractions as influenced by beating (Fig. 13) show that the virgin pulp is better than the recycled ones.

About 70 per cent of the decrease in this index is due to the beating of the virgin pulp. This causes, apart from a slight decrease in breaking length, not only some shortening of fibres, but, more importantly, a considerable increase

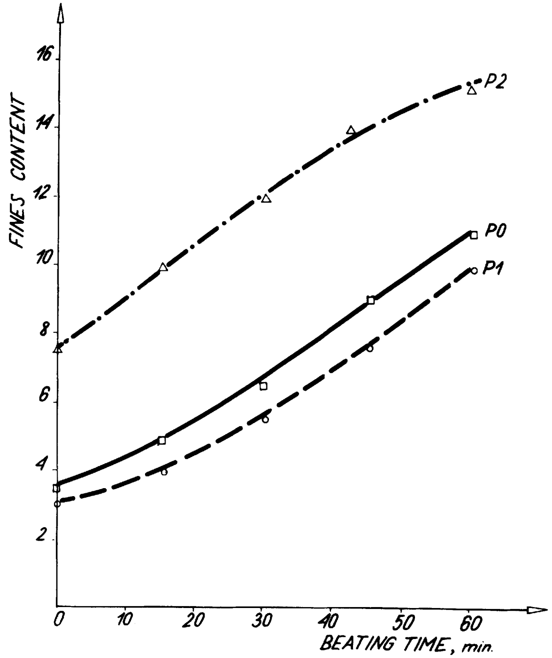

Fig. 9—Effect of beating model pulps on their fines content

in the fines content of the recycled pulp. This, of course, strongly influences the tearing strength.

The negative changes in this index, caused by forming and drying, are mainly due to changes caused by these processes upon the fibrous fraction. The change in the fines compensates to a small extent.

Generally speaking, it is the changes in the fibrous fraction of the virgin pulp, which take place during recycling, which have the greatest influence upon the deterioration of the tear/tensile index.

Taking now the third concern—that of the effective papermaking capability of these experimental pulps—we may consider the changes in breaking length as a function of pulp wetness. In comparing pulps, the best indication of real papermaking capacity is the achievement of high breaking length at low wetness.

This ‘papermaking index’ has some relationship to the ratio of tensile strength to wetness. The higher the better.

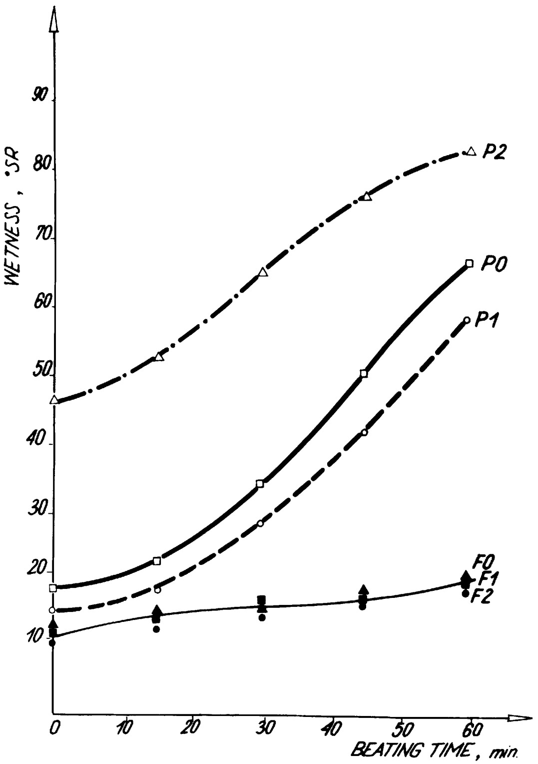

Fig. 10—Effect of beating model pulps on the wetness of these pulps and of their fibrous fractions

Referring to Fig. 14, it is apparent that the typical recycled pulp R2 is inferior to the virgin pulp PO from which it originates. The main reason for this is the beating of the virgin pulp which greatly increases wetness whilst, at the same time, decreasing breaking length. The forming and drying processes contribute to a lesser degree because they cause a decrease of both factors.

Recapitulating the results from the third set of experiments: The influence of the forming, drying and beating processes are identified in their effects upon paper made from the recycled material. The beating of the virgin pulp is dominant in increasing the fines and wetness of the recycled pulp. It also has a major bad effect upon the tear strength and the tear/tensile index. Furthermore the 'papermaking index' (tensile/wetness ratio) is significantly affected by the beating of the virgin pulp.

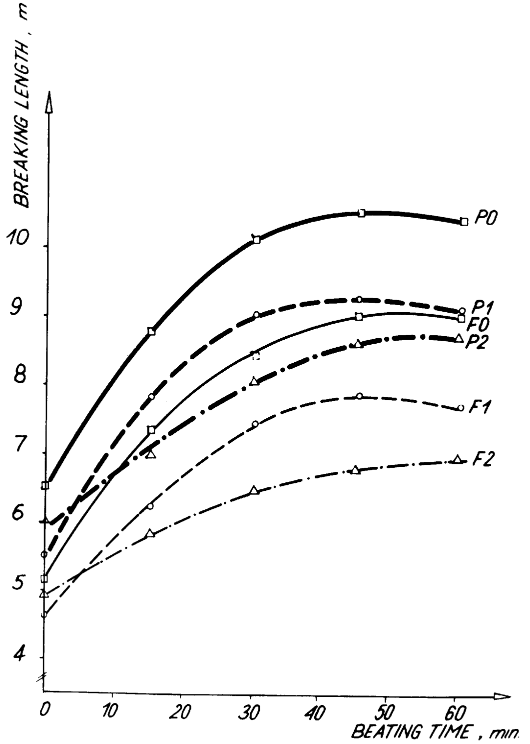

Fig. 11—Effect of beating model pulps on the breaking length of these pulps and of their fibrous fractions

Forming and drying of virgin pulp plays a conclusive part in decreasing the WRV of recycled pulp as well as the breaking length and tear strength of the paper subsequently made from it.

To a lesser degree the forming and drying processes also worsen the tensile/tear index and the 'papermaking index'.

Analysis of the parts played by the two fractions of the recycled pulps suggest that the fibrous fraction dominates in decreasing WRV, breaking length, burst and the ratio of breaking length to tearing strength of paper.

Changes in both fibrous and fines components cause, to a greater or lesser degree, a decrease in tearing strength. Changes in fines affect conclusively only the increase of the pulp's wetness. However, this characteristic constitutes the biggest barrier to rational regeneration of strength.

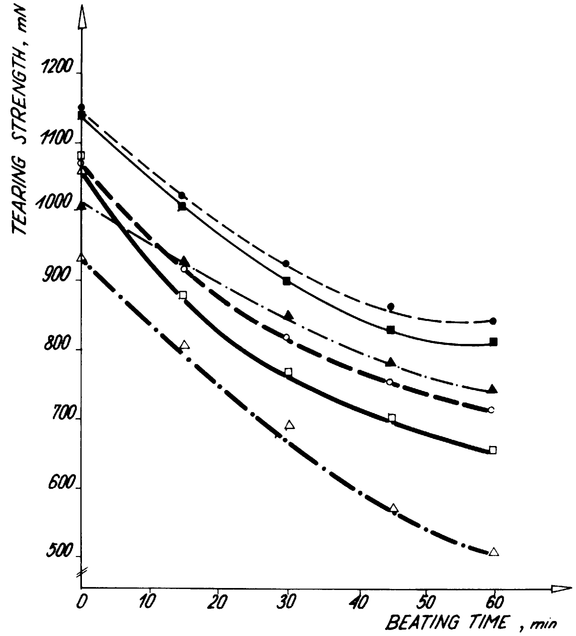

Fig. 12—Effect of beating model pulps on the tearing strength of these pulps and of their fibrous fractions

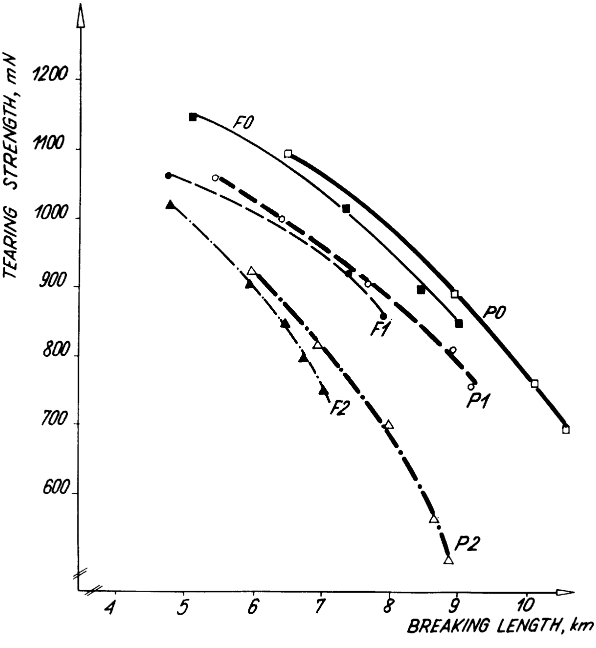

Fig. 13—Relation between breaking length and tearing strength of beaten model pulps and their fibrous fractions

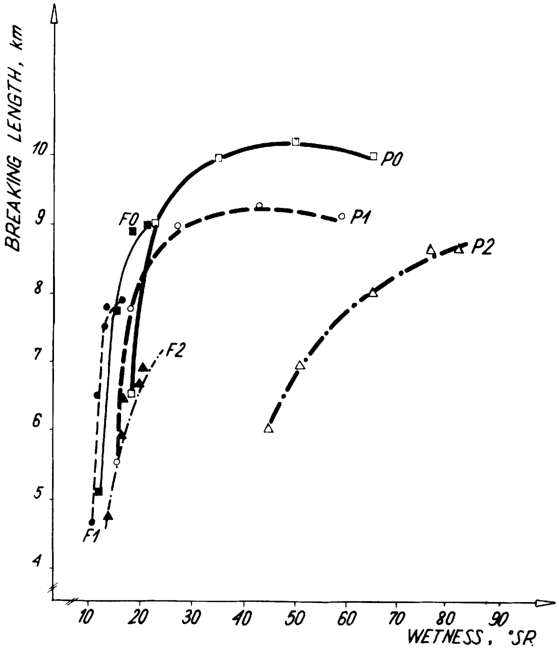

Fig. 14—Relation between wetness and breaking length of beaten model pulps and of their fibrous fractions

It now seems obvious that recycled pulps must be thought of as heterogeneous mixtures of two fractional components. Each of these components are influenced in different ways by the processes through which they pass. This approach can lead to the development of new, original methods for the production of strong papers from recycled pulps.

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Discussion

Dr E. L. Back We have heard a couple of times this morning the word 'hornification' and I think it is very worthwhile to try to understand what it means on a chemical basis. What I put forward is a personal understanding based on quite a lot of work we did years ago, but also published in the literature. My understanding is that there are three fundamental reactions. The first one is the auto-crosslinking reaction in cellulose fibres which produces the swelling restrictions. This reaction takes place with time and naturally it takes place much more rapidly at higher temperatures. So, although the drying time is short, a substantial reaction can take place. The second reaction is the re-hydrophobation of cellulosic surfaces due to redistribution of olefinic materials, such as fatty acids, as was very nicely shown 20 years ago by Dr Swanson of the Appleton Institute. This reaction takes place due to the resinous material which is initially in the pulp or also can take place with rosin sizes, resin acids which have been added during the sizing operation. The third reaction is the hydrolytic breaking of covalent bonds in the chains of the cellulose. These three reactions can be shown in a number of model experiments. For instance, if someone does not believe in auto-crosslinking it is easy to show that, if all the carbonyl groups in the paper have been taken out (by reduction with sodium borohydride for example) the auto-crosslinking is through the wet strength, either in the direction of the paper or in the z-direction, and it is well-known that all aged papers have considerable wet strength. This is just one way to say that there are swelling restrictions. There are a number of catalytic effects for this auto-cross-linking and people working with electrical papers know them quite well. We have firstly the acidic catalysis of the auto-cross-linking which takes place due to acid salts added in connection with sizing as an aluminium sulphate and also due to the absorption of sulphur dioxide from the environment which in the paper is oxidised to sulphur trioxide (as shown about 20 years ago by Drs Grant and Hudson here in Manchester). We also have the acidic catalysation due to carboxylic groups. Whenever the carboxylic groups are blocked with for instance divalent groups such as magnesium or calcium, the paper becomes

Under the chairmanship of M. I. MacLaurin more stable. It is a common process in production of some technical papers. I think understanding these things makes it more easy to understand what to do. Cross-linking, swelling restrictions are there and any means to improve swelling including chemical means, will be helpful. The rehydrophobation is a reaction which is most important in the first cycle because the fatty acids slowly oxidise because many of them are unsaturated fatty acids, and then the material becomes more hydrophylic on ageing. The chain-breaking makes the material more brittle and more susceptible to any type of very strong beating, thus very careful beating can prevent some of the production of fines due to the embrittlement caused by the breaking of cellulosic bonds.

Prof. H. W. Giertz The paper I gave at the 1965 symposium (Consolidation of the Paper Web, London 1966, 59–83) has some bearing on this discussion. It dealt with swelling and restricted swelling as mentioned by Emerton in his book on beating (H. W. Emerton, *Fundamentals of the Beating Process*, The British Paper and Board Industry Research Association, Kenley, 1957). The question of dried-in strains was also discussed in that paper.

Dr D. A. I. Goring The classical answer is because it is a well ordered hydrogen bond system and of course the molecules are very long and the energetics are such that water is not able to break all the hydrogen bonds. My question to that answer would be 'why is cellohexose or celloheptose insoluble in water?' That's only 6, 7, 8 glucose units long and I would like to suggest a line of thought which perhaps the material scientists, who sometime deal with cellulose, have not followed up (as far as I know of, except in one case and this is a work of Warwicker). The point I would like to make is that, if you make a model of cellulose and lay it on that table in front of the panel, what you would see is a hydrophobic ribbon, that is, a sort of cyclohexane-type ribbon and on the edges you would see hydroxyl groups, and this particular structure must exist in the crystal and therefore in the crystal one would have of course hydrogen bonds and these would perhaps no doubt be the main energetic links keeping the molecules together. In addition to this, you would have Van de Waals forces, the kind of forces that keep cyclohexane molecules together, between the cellulose molecules and I suspect that when a strongly hydrogen bond-breaking solvent like water attacks cellulose and swells it, that a fair amount of the cohesion left in the cellulose is due to these Van de Waals forces between the hydrophobic regions of the chain and that when an oily solvent, such as Toluene or Hexane spreads on cellulose, that the forces hold together because of the hydrogen bonds. But the one point I would like to make is that perhaps in the cellulose fibre itself, and indeed in the bonding between cellulose fibres the non-hydrogen bonding Van de Waals forces do play a part.

Prof. R. Marton We have been talking all morning about pulp recycling. I assume we are talking about kraft pulp recycling. However, I want to bring to your attention a little work which we have done and this refers to paper recycling. Very seldom do we recycle pulps in the industry—we recycle papers—and if we recycle papers, such as newsprint, it is only 15 to 20 per cent chemical pulp, the rest being mechanical pulp. Now, all these different pulps recycle differently. Kraft pulp would recycle as we have heard today. Sulphite pulp recycles differently—it degrades even more or loses more strength than does the kraft and, if you take oxygen pulp, it loses five times as much strength as does the kraft pulp. However, the main component of newsprint (the mechanical pulp groundwood or thermomechanical or refiner groundwood)—all high yield pulps, gain breaking length and they gain opacity on recycling. So I would suggest let's not over-simplify the whole business of recycling. Let's study each component separately because each component behaves differently. In addition you have to differentiate between softwoods and hardwoods.

Dr A. H. Nissan I would like to make two comments, one on Dr Back's remarks. These are extremely important and what I want to add is that they are very fast reactions and they are in the first place very much on the surface. Working on the basis of Dr Back's previous findings, we developed in Westvaco a technique for studying this and, in fact, we obtained a Canadian patent on it (but it did not prove of commercial value). You can actually take a sheet of paper, which is printed, put it into a Xerox-type machine, put paper underneath and, if you project heat on the printed sheet, the difference in the temperature produced on the surface of the paper (because of the difference of the reflection of the heat from the printed sheet) is enough, in the time that it takes for a Xerox machine to work, to produce surface hornification with less water absorption on the areas so affected that, when you put it in a uniform electric charge, you get a pattern, a virtual pattern, straight on to the sheet of paper. If you then put it into a toner and print it, you have what we call the Fax machine. Now I have to apologise to Dr Corte. It does not only work with paper. You may take a cotton handerkerchief and you put it through, print it and it works the same way. So it is cellulose and not the other components only. Presumably hemicellulose would be more reactive (presumably, but we do not know) but it can work on ordinary cotton cellulose, and, you can get printed sheets, which means that these reactions that were described a few minutes ago (the part of the auto-catalytic reaction within the surface of the pulp) are fast due to heat. We proved that it was the heat by taking a wire in the form of an A, or B or what have you, bringing it to as low as 95° C (Celsius), stamping it on the paper for a second or so, taking it away, pushing it through a uniform electric charging system, shake it, leave it three days, take that and put it through a toner, it reproduces the shape of the thing. So it is a permanent thing, presumably in time it would dissolve. So these reactions are important. They are fast and they work at drying temperatures. You don't have to go to very high temperatures. Another thing is in answer to Dr Goring, 'why doesn't cellulose dissolve in water', there was a paper in that very important year 1957 in the transactions I think of the Faraday Society. It was a remarkable paper because according to that author, of all bonds, the hydrogen bond is peculiar in this way. It occurs with other bonds but apparently for some thermodynamic reasons I do not remember, it is peculiar to hydrogen bonds and very important because it explains why cells in living organisms have identity which is controlled by the hydrogen bond. The point that I wanted to demonstrate is this: If you take N bonds in series, the energy required to unzip them like a hook from a zipper successively—not simultaneously—provided you make the restriction that you have to unzip all of them before they separate, is N times the energy of a single bond. So you can see that a long chain, a zipper of hydrogen bonds will require very high energy to unzip them completely. You will unzip a few of them and they will rejoin again because they zip up again. It was a thermodynamic mathematical paper and that tended to explain why, for example, even 2½ normal sulphuric acid leaves crystallites intact. Whether further experiments have been done since then, I have not followed and I really don't know but there was this paper, I believe it was around 1957, but I am not sure when.