Some Recent Trends in the German and European Pulping Industry

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INTRODUCTION

In this paper, a short review shall be given about recent trends in the pulping industry in Germany and the surrounding parts of Europe. Further, some ideas shall be laid out which have come up in connection with the new orientation of our institute, which has been changed from Celluloseinstitute to an Institut fur Makromolekulare Chemie. This means the integration into polymer chemistry as such, cellulose is understood as a macromolecule. though a very important one, and the knowledge and experience of polymer chemistry in its broadest sense shall be used in connection with further developments on cellulose. The discussion will deal separately with the different branches of pulping, and then atempt to derive conclusions.

RAW MATERIAL — WOOD

An interesting new feature is the fact that planting of fast growing woods takes place on a large scale in southern Europe, mainly Portugal and Spain. It is mainly Eucalyptus, which concerned (E. regnans, E. camaldulensis, E. globulus, E. saligna). Since this type of wood may be cut already after about 20 years, we may expect that these plantations will come to bear in the not too far future.

In central Europe, and in Germany, the raw matetrial situation is somewhat tight. More and more attempts are made to increase the use of splinters and wastes (sawdust). Furthermore, there seems also to be developing the need for a new attitude in forestry. It cannot be neglected that the pulp and paper industry is a big consumer of wood, and the forestry officials should take notice of this fact. Thus it would be desirable, that in the replanting policy pulp experts should be heard. Wood growing is no more justified as a means merely to renew and protect the woodland, but also as the production of an important raw material, and it is only adequate that the main consumers should be heared.

Some words can be said about the chip storage. It is true, that e.g. for sulfite pulping it can reduce the storage time from 1 year to 6 - 8 weeks due to the accelerated pitch decomposition. On the other hand, the chips are more amenable to microbial attack, which can bring about significant losses. The use of pesticides is recommended as a remedy.

SEMICHEMICAL PULPS

With regard of semichemical pulps, the big expectations of several years ago did not come true. This may be caused by a divergent development of the wishes of the consumers; in central Europe the market calls for soft pulps; in order to comply with this the semichemicals must undergo severe bleaching, and thereby we loose again what we have saved by the high yield pulping. Still there are some fields for which semichemicals have their place. Concerning the pulping method. it is mainnly the NSSC procedure which is being used; due to the reduced or eliminated hydrolysis, the hemicontent and thereby the yield is enhanced. Semichemical pulps are still a "must" in corrugated medium (fluting paper), birch is best here. As an example for recent applications in this regard, some experiments perform ed in a continuous Escher-Wyss pulper (with preimpregnation) may be cited(1). It was possible to pulp mixtures of softwood (beech etc.) with about 15% spruce for use as fluting pulps. 72-75% yield could be obtained. During these experiments, the bases Mg. Na, and NH_4 were used. While the Magnefite and the NaNSSC method proved to be nearly equivalent, the NH_4NSSC process yielded slightly better results: delignification rate was higher, the selectivity of delignification was better, and the beating expenditure required was lower. Thus the NH_4 cation seems to be superior in some regards. In the same experiments, beech sawdust was pulped and used for a 65% addition to artificial parchment. Poplar, birch etc. were pulped to ultra high yield pulps, which could be added to e.g. newsprint in an amount of 15%. A yield of 85% could be obtained. The authors state, that a yield of 90% appears possible Chemimechanical pulps of such a high yield will, however, already approach mechanical pulps (groundwood) in some properties.

PULPING AND PULPING METHODS

Before discussing the two main methods, sulfite and sulfate,it may be appropriate to tabulate some of the features and properties of the pulps obtained by these two

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methods. This has been tried in the following **Table I.**

It is interesting to compare the percentages of sulfate mills in differtnt parts of the world. The data are :

World :	2/3	Sulfate
USA :	3/4	Sulfate
Europe :	2/3	Sulfate
W. Germany :	practically no sulfate	

Now we shall discuss both processes separately.

Sulfite pulping

Although this pulping method undergoes a general recess on a worldwide scale, it still is practically the only one used in W. Germany; the reason for this is mainly the tradition of this method in our country, and the reluctance to erect sulfate pulp mills for fear of odour trouble. Still it is an open question why this method receeds in spite of the higher variability of end products (tailor made pulps), easier beating, better sheet formation, better whiteness and color reversion stability, and good opacity (though not so good if high strength is required). The answer must be that sulfite pulping is too selective, it accepts only certain woods (the "sulfite woods"). On tht other hands, sulfate pulping takes any wood and is therefore better equipped to meet changes in the availability of material. Thus we may record, that on a world wide scale in the last 10 years 139 completely new sulfate mills have been erected, but only 10 sulfite mills. The traditional Ca-bisulfite process, which

Table I : Comparison of the two main pulping methods

	Sulfate	Sulfite
Price	More expensive	Cheaper
Raw material	All types of wood	Only "sulfite" wood : spruce, beech, birch, poplar etc. Difficulties with pine, oak, douglasie.
Suitability for Rayon pulp	High-alpha pulps (prehydrolysis) for tire cord. Only low viscosity pulps	Cheap rayon pulps; beech pulps for staple fiber. High viscosity pulps
Pulp for nitration, etherification		Preferred on price grounds. For ethers high viscosity pulps
Fillers, plastics		Preferred due to better color reversion stability
Artificial parchement	Semibleached sulfate pulp receeding due to high price	Preferred due to lower beating expenditure
Addition to newsprint		Unbleached sulfite of not too high yield, weakly acidic pulping (e.g. Magnefite); may replace sulfate due to its lower price.
Cardboard, Kraftpaper	High yield sulfate	Sulfiteliner too brittle
Paper properties Strength	Good. tear strength excellent. Hardwood strength approach sulfite	Great variability, tear strength inferior to sulfate.
Volume	Higher	Denser paper;
Whiteness	maximum 92%, only with top qualities	Extreme whiteness obtained with moderate ClO_2
Color reversion stability		Better
Opacity	Higher	High opacity with soft pulps, not compatible with high strength
Sheet formation	Not so good; can be improved by admixture of short fiber pulps	Better

uses a very low pH (around 2), is being competed by the new soluble base methods.

A few words may be in place about the new soluble base methods. In many a regard ammonium is a very suitable base, but it cannot be recovered, the base itself is lost. With sodium, the base Na can be recovered, but the recovery is complicated and expensive. It is, however, advantageously used in the NSSC process for semichemical pulps; the new chemomechanical pulps can be obtained with a 85% yield; softwoods can be pulped to give admixtures for newsprint etc. The possibility of continuous pulping should be stressed, the two stage methods mentioned. Further, mention shall be made of its versatility, including the easy adaptability of the equipment to sulfate process. For the magnesium base elegant recovery methods are available now, which yield up to 90% recovery (cf.(2)). However, Mg. recovery requires an incinerator of special design. In the magnesium bisulfite process the pH is lowered to 2 during cooking. To keep it at 3-4, MgO is added or SO_2 is degassed. Thus strong pulps are obtained. The high yield is due to the slow hydrolysis, which brings about higher hemi content and thereby higher strength. The method of degassing SO_2 is used in the well known Magnefite process, in which a somewhat high temperature (above 150°C) is required to pulp fast enough. Again more hemi, thus higher yield and better strength is obtained :

Here the question may be raised: what is a "good" pulp? It is clear, that quality cannot be defined once and for ever, since for any end use a different "quality" may be adequate. In USA the call is for soft sulfite pulps, while in general strong high yield pulps of high density are wanted. Therefore it is legitimate to ask about the meaning of the term "quality". A new view in this regard has been taken in recent time: a high quality pulp may have any properties, but these properties must be highly constant. So the uniformity of properties, and their constancy in the progress of time, is the aim which should be strived for. This new quality notion can be best realized by means of continuous processes.

Here we enter a new field of high importance. There is little doubt, that in future the general development will be in favour of continuous methods. This holds not only for the pulping industry, but for most other industries too. It is not only the higher uniformity of end products, but also the possibility of extensive automation which makes for the superiority of continuous methods as compared with batch processes. An important example has been set in this regard by the new continuous Waldof pulping process, which has been installed recently. It is the acidic bisulfite process with magnesium base, performed continuously in Kamyr equipment. The following 5 stage bleaching with diffusion washing is also done continuously. A recent paper (3) says that the new pulper produces 200 tons/day. The pulping zone is 32 meters long, the stay of the wood chips in the pulping zone lasts 4,5 hours. The ratio wood/acid is lower, the chemicals concentration higher as compared with the usual batch pulping. The continuous method allows for better control in the reactor, though highly sophisticated control devices are required. The pressure in the pulper is controlled via the vapor tension of So_2 and Co_2. The mentioned paper states, that, in comparison with a pulp prepared by orthodox methods, that, a continuously produced pulp is (for the same viscosity) better digested, but still of higher hemi content. Thus the digestion appears to be more selective. The yield is higher (e. g. 50%vs. 45%). Strength properties are better, and the pulp is very uniform. The continuous method reguires less steam, but more energy. The final aim of these continuous methods is an automatic pulping process. This would, of course, require automatic feedback control for the reaction zone. To achieve this, we must first fully master the chemistry of pulping; one reason more why fundamental studies into pulping chemistry are still very important.

Sulfate pulping

With regard to sulfate pulping, there is next to nothing in Germany. The main reason for the failure to erect sulfate pulp mills is the fear of odor troubles, which comes to bear in the respective legislation, although it has been shown in other parts of the world that odor trouble is a problem which can be dealt with quite satisfactory. Some changes in this attitute may be ahead, even if not for the immediate future.

The general trend here too is for continuous pulping (Kamyr) on the one hand. On the other hand, strong pulps appear to be in favour now, as they undergo less degradation in bleaching, have better strength properties, high yield, and short fiber pulps with optimum strength can be produced. In order to comply with these items, the "peeling" reaction must be avoided. It is known, that in sulfate pulping the yield is decreased due to alkaline degradation starting at the carbonyl chain ends ("peeling reaction"). Therefore, to improve matters, these terminal groups must be either oxidized or reduced.A reduction is posible by means of Na-borohydride, which brings a yield increase up to 10%. But this method is too expensive. Hydrazine and hydroxylamine have been tried too. A cheaper method is the empirically found use of a pulping liquor of higher sulfidity — either sulfur or Na-polysulfide is added to the pulping liquor. Up to 5% yield increase are obtained. The mechanism is probably an oxidation of the carbonyl terminals. In any event the polysulfide method has now a secure place. The digestion occurs at 140-160°C (usual sulfate process 170°C); the pulping time is longer. In the two stage poysulfide process the chips are impregnated with Na-polysulfide in the first stage at 110-130°C, and in the second stage the digestion is carried out under usual conditions. In another new method, a preimpregnation is made with H_2S gas at 10 at, then a usual digestion follows. This method is said to bring about up to 7% increase in yield. But it still is in the experimental stage.

Again it must be added, that some significant increase in sulfate pulping is to be expected within the next two decades for Europe. Already now Western Europe is producing 0,3 million tons per year of mainly short fiber sulfate pulps, Portugal makes 0.4 million tons per year of sulfate pulp (eucalyptus and pine) of excellent quality; W. Germany produces 0,7 million tons per year of sulfite pulp. As soon as the new plantations on the iberian peninsula (mainly Portugal) come to bear, we may expect a true boom in the European short fiber market. In 10 years from now Portugal may be able to produce 1 million tons per year !

BLEACHING

Bleaching has developed into a very sophisticated art, up to 12 stages are being used in the process. The present trend is to reduce the number of stages on the one hand, on the other hand it is tried to devise bleaching methods which avoid degradation and losses: one should not loose during bleaching what one has saved during pulping. Even more so, since the bleaching losses are irreversible, while the pulping losses can be compensated in part by the recovery processes.

In the delignifying methods (C1, hypochlorite, ClO_2) attempts are made to reduce the number of steps and their duration. Furthermore, certain degradation reducing additives have been detected; an example is sulfamic acid (4), which prevents degradation and thus reduces the carbohydrate loss if added at the hypochlorite stage. Further new developments are fast bleaching methods with higher pulp consistency (20-30%) making use of gaseous chlorine or chlorine dioxide, followed by extraction with NH_3-gas. In this way, a 45 minutes bleaching is as good as an orthodox 5 stages bleaching which lasts 10 hrs. However, this method is still being developed. Further we must mention the alkaline oxygen bleaching (O_2-gas), it is used with 15% consistency, 130°C, and 10-12 at gas pressure. Again the bleaching time and the number of stages are drastically reduced. Peroxyacetic acid is being used experimentally for semichemical pulps.

Non-delignifying bleaching (Na_2O_2, H_2O_2 for oxidation, Zn or Na-dithionite for reduction) are gaining some ground in the field of mechanical pulp (groundwood) and semichemicals. Their capacity to reduce color reversion is certainly an advantage. Considerable development work is under way in this field, especially for H_2O_2(5). New methods and additives are sought, which can prevent color reversion by stablization of non chromophoric groups, and which also convert the residual lignin to a suitable and colorless form.

Continuous methods are also being developed (Kamyr), this fits with the general trend to continuous methods with the perspective of automation.

SOME FUNDAMENTAL CONSIDERATIONS

If we talk of "high yield" it is reasonable to pose the question: what is high yield? Obviously, we wish to recover all cellulose fibers, and as much as possible of the hemi portion and of the lignin, but in a form suitable for papermaking. A yield increase is thus only possible on account of hemi and lignin. It is not enough to recover e.g. the complete hemi content, rather the hemi must meet certain requirements. This holds even more if we try to retain some of the lignin. Here the problem is, whether it will be possible to transform lignin into a suitable form, which can be retained in the paper without detrimental effects. That means again, that we should study lignin chemistry and all the modification reactions which can be done on lignin.

In some recent papers, Kleinert (6) has stressed his findings that during pulping reactions free radicals are formed. In sulfate pulping, the bulk delignification occurs over free radicals, and in order to guarantee easy lignin removal, secondary condensation reactions must be avoided. In neutral sulfite pulping too free radicals have been found; Kleinert conjectures that in this case lignin may be grafted to hemi. He suggested the use of free radical scavengers to prevent secondary condensations, which could lead to insolubilization of lignin. The degradation of hemi too involves free radicals, and whenever lignin is grafted to hemi, a certain hemi degradation must take place in order to remove the lignin. With sulfate and acidic sulfite pulping strong hydrolysis of hemi takes place. If lignnin is grafted to hemi, the removed lignin should have carbohydrate endgroups, as it has actually been found. However, these endgroups may also be residuals from the original hemilignin bonds.

These ideas call for detailed investigations. The more so, since the transient existence of free radicals suggest the use and application of techniques which have been developed by polymer chemists in their polymerization studies. One should use suitable monomers as models, for instance as radical scavengers. If easily analysable monomers are used, the free radical sites could be studied in detail — though there existence has been proved beyond doubt by the elegant ESR-experiments by Kleinert. It is known, that polymers may play interesting roles as additives in pulping, e.g. in combination with other compounds for the stabilization of sulfite pulping acid. After all, the polysulfides, which act so significantly in alkaline pulping, must be regarded as polymers too! Finally, it may be mentioned, that for the color reversion reactions too free radicals may play a role, and that in the course of color reversion both graft copolymerization and depositing polymerization may occur (7). Here too model experiments with suitable monomers may prove informative.

In sulfate pulping, alkali is consumed for the neutralization of low molecular weight acids formed. One might try to perform this neutralization by cationic polymers, this would save alkali and enhance the yield.

To increase the yield in pulping, one has three possibilities:

1. Avoid carbohydrate losses
2. Make lignin useful
3. Add cheap and suitable monomers

While point 1. and 2. are familiar and curently used, point 3. is new, and next to nothing has been done in this regard. Here we have a completely new field for experimentation, although it might depart somewhat from orthodox papermaking. During pulping, both cellulose fibers and hemicellulose may be partners of

1. Readsorption of hemi (e.g on pH decrease in sulfate pulping)
2. Repolymerization (condensation) of carbohydrates and lignin
   - 2.1 Depositing polymerization (lead to inclusion)
   - 2.2 Graft copolymerization (leads to chemical bonds)

Both secondary polymerization proceses may increase the yield. As a possible, though at present somewhat utopistic goal it may even be feasible to arrive at a yield of more then 100% by addition of suitable monomers. Although at present we are far away from such results, it still is time to explore the potentialities of secondary polymerization processes initiated by the addition of monomers. Of course it has to be tried out, at what stage these monomers should be added, and what monomers are most promising. The field is completely new, and there is next to nothing available in literature. It will be hard to tell how such a "marriage" between cellulose and synthetic polymers will influence the paper properties, apart from the fact that certain special features (water repellency, inflammability) could be added. But this is trivial, more interesting are the changes which could be expected in the mechanical properties. Here we may imagine that coiled, elastic linear chain molecules with a type of lateral bonding similar to that found in cellulose, could take up stress peaks which would otherwise destroy the paper Durability too, e.g. in flexing, could be improved. In general, we should not stick to the question: how can we improve paper, but should rather ask: how can we produce a material which is superior to paper. It is our strong opinion, that the possibilities of synthetic polymers should be tested on a broad scale.

The ideas layed out in the foregoing call for a good understanding of both pulping chemistry and polymer chemistry. Only if these conditions are met, we may try to follow this new approach, including the potential possibilities of polymers. Its eventual aim will be the integration of cellulose and wood chemistry into the broad science of macromolecules.

LITERATURE

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Need for a Viable Forest Policy

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In the modern Industrial Era, a large number of industries depend on forest products as their raw materials. There are three major categories of Industries which are utilising various forest produce. They are:

1. Pulp and Paper Industry,
2. Plywood, Hardboards, Insulating Boards Industry, and
3. Match Box Industry.

Over and above this, the use of Timber is also valuable for domestic and packing purposes. The demand from the industries is increasing sharply and the Pulp and Paper Industry alone has already made rapid progress and is expanding very fast in an astounding manner by the proposed planned production programme of increasing four-fold from the present rate of production, that

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