

PLASMA-INDUCED ADHESION IN CELLULOSE AND SYNTHETIC POLYMERS

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Synopsis The papermaking bond between cellulose surfaces can be increased markedly by pretreatment of the surfaces in a corona plasma in oxygen or air. The effect is probably due to oxidative degradation of the molecules of cellulose near the surface. Similar increase in bonding can be achieved by treatment with ozone gas. This is the basis of the Paprizon process, in which paper made from mechanical pulp is brightened and strengthened by pretreatment with hydrogen peroxide and ozone.

When two surfaces of a thermoplastic such as polythene are pressed together at elevated temperature, autohesion can take place. Pretreatment of the surfaces in a corona plasma lowers the temperature at which autohesion occurs. This effect is probably not caused by surface oxidation, since it can be produced by both oxidising and non-oxidising plasmas. Its origin is uncertain, but a possible explanation is that the discharge causes electret formation in the polymer sheet, which promotes autohesion by facilitating interdiffusion of the polymer molecules on contiguous surfaces. Autohesion of thermoplastics will be most important in processes such as pressing and calendering of sheets containing the new synthetic fibres.

Preliminary results have indicated that effects similar to those described above may be obtained by treating cellulose and polythene surfaces in a microwave plasma. The advantage of using microwave energy is that the plasma can be made to fill the entire volume of the treatment chamber, rather than being restricted to a short spark as in the case of a corona discharge.

The thermally induced bond between cellulose and thermoplastic polymers is increased also by pretreatment of the surface in a corona plasma. The effect is usually most marked when both surfaces are treated, but treatment of the polymer alone will produce a good bond. For wood/polymer adhesion, it is possible to produce a bond equivalent to that obtained by use of a conventional plywood adhesive by pressing a thin sheet of corona-treated polythene between two sheets of woody veneer.

Hardboards can be made by hot pressing an air-dry mixture of wood fibre with a finely powdered polymer. Treatment of the polymer powder in a corona plasma,

Under the chairmanship of Dr H. Corte

before mixing and pressing, produces a substantial improvement in both the strength and water resistance of the finished board. It is possible to make a board of pressure-refined aspen fibres and powdered polythene, which is as strong as conventional hardboards, but which shows about one third of their dimensional instability on soaking or boiling in water.

Introduction

THE paper industry exists because certain surfaces can be made to stick together. For example, the cellulose interfibre bond is the basis of the paper-making process. In sizing, coating, laminating and glueing, adhesion plays a dominant role in the manufacture of the final product. Thus, any method by means of which cellulose or synthetic polymer surfaces may be made to become more adhesive holds important implications for the industry.

One such method is to treat the surface in a corona plasma before making the bond.⁽¹⁾ A cellulose sheet passed through an electrical discharge shows better adhesion to thermoplastics⁽²⁾ and the printability of polythene is improved by such treatment.⁽³⁾ Greene has shown that corona treatment enhances the adhesion of melt coatings to paper.⁽⁴⁾

Certain aspects of the cold plasma treatment of cellulose and synthetic polymer surfaces have been investigated for some time in the author's laboratory.⁽⁵⁻¹¹⁾ The present paper is a review of the highlights of this work. An attempt will be made to give an explanation of the phenomena observed. In addition, the significance of the findings to some possible applications will be discussed.

The water-induced cellulose bond

THIN strips of cellulose material were treated in a corona plasma in oxygen gas or air. After treatment, the strips were wetted, pressed together wet and dried under pressure. The bond thus formed was tested by clamping the specimen as shown in Fig. 1 and breaking the bond in shear.

It was found that treatment of the cellulose surface in the discharge produced a marked increase in the water-induced bond. This effect is shown in Table 1 for three types of strip-deacetylated cellulose acetate, sulphite pulp handsheets (4 times the usual grammage) and 0.02 in birch veneer. The strips were 2 mm wide and the conditions of treatment were 15 000 V at 60 Hz for 15 min in oxygen gas.

What is the cause of this remarkable effect? By infra-red analysis, it can be shown that the corona treatment oxidises the cellulose. Microscopic examination also reveals surface degradation. Thus, it seems likely that the discharge will produce on the surface a layer of oxidised and degraded cellulose macromolecules. These hemicellulose-like fragments will tend to swell in water and

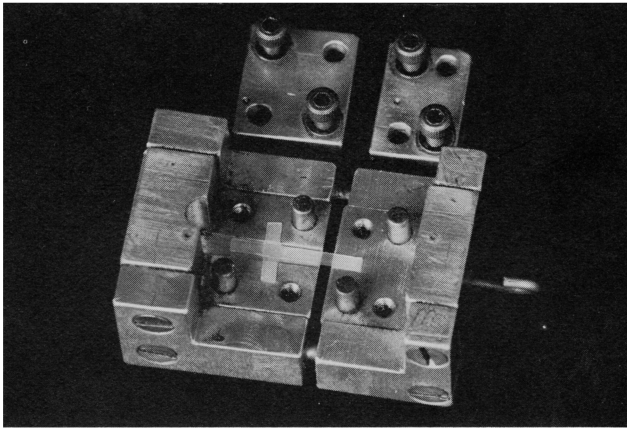


Fig. 1—Clamping of bonded specimen to allow rupture in shear

form a layer of glue that will enhance the bonding of the surface. A similar explanation for the effect of corona treatment on cellulose has been proposed by Brown & Swanson, who relate the enhanced bonding to changes in the solid surface free energy accompanying the treatment.⁽¹²⁾

TABLE 1—EFFECT OF CORONA TREATMENT ON BOND AND TENSILE STRENGTH

<i>Sample</i>	<i>Bond strength,</i> <i>kg/cm²</i>	<i>Tensile strength,</i> <i>kg/cm²</i>
Cellulose: Treated	75	1 400
Control	11	1 500
Handsheet: Treated	51	710
Control	2	750
Birch wood: Treated	16	850
Control	1	940

It is important to note that the degradation is restricted to the surface and does not appear to affect the bulk properties of the strips. This is apparent from the results in Table 1, which show that the treatment produces only a small change in the tensile strength of the strip.

It seems likely, though not certain, that ozone is the active agent in the treatment of cellulose in a corona discharge. Ozone is produced in a corona discharge⁽¹³⁾ and is known to degrade and oxidise cellulose.^(14–16) Thus, if the treatment consists of nothing more than ozonisation, it should be possible to produce similar effects by reacting a cellulose surface with the gases effluent

from an oxygen discharge. This was done and, as shown in Table 2, an enhancement of adhesion could be produced.

TABLE 2—EFFECT OF 15 min TREATMENT WITH OZONISED OXYGEN ON BOND STRENGTH

<i>Sample</i>	<i>Bond strength, kg/cm²</i>
Cellulose: Treated	45
Control	10
Handsheet: Treated	22
Control	4

The results shown in Tables 1 and 2 were derived from model experiments in which 2 mm strips of a cellulose sheet were used to make the bond. A crucial question is whether or not the method can be applied to enhance the bonding of papermaking fibres. Experiments were carried out in which dry pulp fibres were treated in the discharge, soaked in water made into sheets in the usual manner. It was found that rather weak pulps such as flash-dried refiner groundwood gave sheets of up to double the tensile strength after corona treatment of the fibres. Similar results have been obtained by the treatment of pulps with gases effluent from the corona discharge. The Paprizone process developed by Liebergott⁽¹⁷⁾ at PPRIC consists of the treatment of mechanical pulp at 30 per cent consistency with 0.2 g hydrogen peroxide per 100 g dry pulp followed by 1 g ozone per 100 g dry pulp. The effect is to produce an increase of up to 8 points in brightness and 50–100 per cent in the burst factor. It seems likely that the increase in the strength properties of the pulp after the Paprizone treatment is due, in part, to the increase in the bonding produced by the reaction of the surfaces of the fibres with the ozone. Similar increases in strength on treatment of mechanical pulp with ozone have been reported by Soteland & Kringstad.⁽¹⁸⁾

The autohesion of polythene

WHEN a sheet of low density polythene is pressed to a similar sheet at room temperature there is usually no adhesion. As the temperature of pressing is increased, bonding between the two sheets (autohesion) will begin to occur until at 95°–100° C a relatively strong bond is formed. The dependence of bond strength on the temperature of pressing is shown by the curve labelled *control* in Fig. 2.

Thermally induced autohesion of synthetic polymers has been studied in detail by Voyutskii,⁽¹⁹⁾ who has developed the diffusion theory of adhesion to explain the effects observed. When two surfaces of an amorphous polymer are brought into contact, the individual polymer chains begin to interdiffuse.

After a certain interval, the interdiffusion is so extensive that the interface disappears and is replaced by bulk polymer. The rate at which this process occurs depends on the self-diffusion coefficient of the polymer, which in turn depends on the molecular weight and viscosity in the surface layers. With a thermoplastic near its softening temperature (such as low density polythene at 100° C), the viscosity decreases markedly with increase in temperature. Thus, diffusion of polymer chains across the interface is facilitated and autohesion occurs.

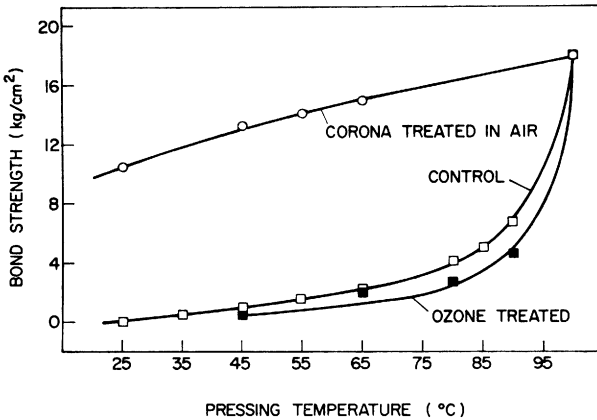


Fig. 2—Effect of pressing temperature on the autohesion of low density polythene: data is given for corona treatment in air, treatment with ozone and the untreated control

If the polythene sheets are treated in a corona plasma before being pressed together, autohesion occurs at a much lower temperature. This effect is illustrated in Fig. 2, which shows that a strong bond can be formed between corona-treated sheets pressed at room temperature. The autohesive bond increases with temperature of pressing, but less rapidly than the control, so that the bond is equal in treated and untreated polythene pressed at 95° C.

Superficially, the effect described above may be considered the thermo-plastic analogue of the corona enhancement of the water-induced cellulose bond. Some important differences, however, should be noted.

1. Water is necessary for the cellulose/cellulose bond; corona treatment of cellulose surfaces did not produce autohesion in the dry state, though polythene surfaces treated in the corona, then wetted, pressed together and dried gave a strong bond.

2. Treatment times required to produce a detectable enhancement of autohesion were much shorter for polythene than for cellulose surfaces—fractions of a second in the former compared with minutes in the latter case.
3. Like cellulose, the polythene surface was oxidised by treatment in oxygen or air (see Fig. 3). When the polymer surface was treated with ozone effluent from an oxygen discharge, however, no enhancement of autohesion was obtained (Fig. 2), even though marked surface oxidation was detectable by infra-red analysis (Fig. 3). In fact, the data in Fig. 2 suggest that surface oxidation reduces the autohesion of polythene. This is the contrast to the adhesion of polythene to metal surfaces, in which oxidation has been shown to increase the strength of the bond.^(20, 21)

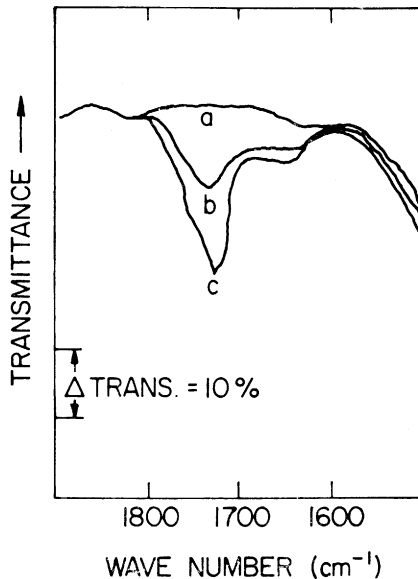


Fig. 3—Multiple internal reflection infra-red spectra of low density polythene—(a) Untreated control (or film treated in nitrogen corona for 30 min); (b) Film treated in oxygen corona for 20 s; (c) Film treated in ozone for 30 min

The band at 1720 cm^{-1} indicates the presence of —C=O groups in the surface layers of the polymer film

When it was found that oxidation *per se* was not important in the enhancement of the autohesion of polythene by corona treatment, experiments were planned in which the effectiveness of the treatment was related to the characteristics of the plasma itself. It was found that the increase in bonding depended

upon the time of the treatment. Yet, if the frequency of the electrical power supply was varied, the bonding produced was simply a function of the number of cycles applied as shown in Fig. 4.⁽²²⁾ Note that the oxidation of the surface became detectable only after maximum bonding had been achieved.

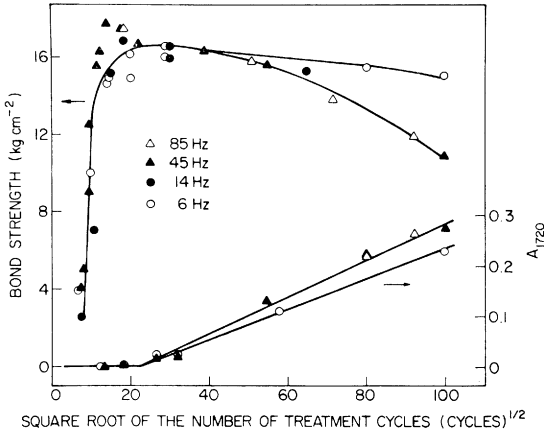


Fig. 4—Bond strength for autohesion of polythene against the square root of the number of cycles for treatments at different frequencies in oxygen gas: the lower curve is the infra-red absorbance at 1720 cm^{-1} (—C=O band) against the square root of the number of cycles

Corona treatment in several gases also revealed the dependence of the effect on the characteristics of the discharge. Enhancement of autohesion was produced by treatment in pure nitrogen, argon and helium, but the time of application required varies considerably in the different gases. Times of treatment in various gases were chosen so that the bond strength produced was equal to 10 kg/cm^2 . Also measured was the electrical power dissipated in the plasma. The results in Table 3 for oxygen and nitrogen show that, although the times of treatment were different, the electrical energy consumed in producing an autohesion of 10 kg/cm^2 was equal for the two gases. A similar effect was found for helium and argon, although here the voltage applied and the energy consumed were lower. These results suggested that the corona-induced autohesion was independent of the nature of the gas, but depended mainly on the voltage applied to and energy consumed in the plasma.

Several possible reasons for the corona-induced autohesion of polythene have been considered, but none permit an unambiguous explanation of the effects observed. It was considered that the enhanced bond strength could be

due to the strengthening of the surface layer by cross-linking, as proposed by Schonhorn and co-workers.^(23, 24) Careful experiments indicated, however, that no measurable gel component was produced even after hours of treatment. Thus, it seems unlikely that the observed increase in autohesion is related to the casing effect.

TABLE 3—TREATMENT TIME IN VARIOUS GASES REQUIRED TO PRODUCE AN AUTOHESION BOND OF 10 kg/cm² FOR POLYTHENE

Gas	Treatment time, s	Potential, kV	Power $\times 10^4$, W/cm ²	Energy $\times 10^4$, W s/cm ²
Oxygen	2.1	19	44	93
Nitrogen	2.9	19	32	94
Helium	27	4	1.9	51
Argon	82	4	0.68	56

A further possibility is that the excited species in the corona cut the polymer chains at the surface of the polythene. This would result in a concentration of chain-ends in the surface, which may facilitate the interdiffusion of polymer molecules across the interface. Yet extremely careful measurements of the molecular weight of the polythene contained in the surface layers have failed to reveal chain scission even after prolonged treatment in nitrogen.

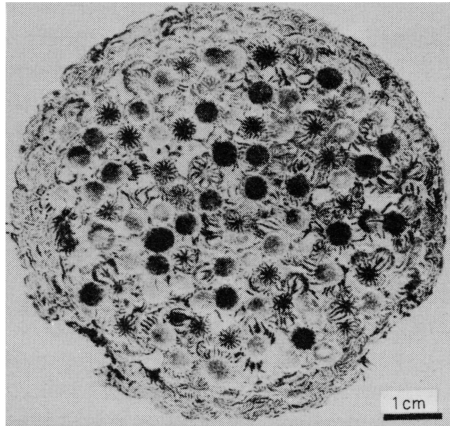


Fig. 5—Lichtenberg dust figure with jeweller's rouge on corona-treated polythene: the treatment was in air and of duration less than 1 s

It has also occurred to us that the autohesion may be enhanced by changes in the electrical properties of the surface. When dielectric materials are subjected to strong electrical fields, charges are induced in the dielectric. This is known as the electret effect.^(25, 26) Electrets can be relatively permanent, sometimes having half-lives of many years at room temperature.⁽²⁷⁾ The charge pattern can be detected by spreading a light dielectric powder on the electret. Such patterns are called *Lichtenberg figures* after the man who discovered them. An example of a Lichtenberg figure developed on the surface of corona-treated polythene is shown in Fig. 5. It is not envisaged that the bonding is established by simple coulombic attraction. Perhaps the charged matrix produced on the surface enhances the interdiffusion of polymer molecules when the surfaces are pressed together.

Treatment in a microwave plasma

WHEN microwave energy is channelled through a gas under certain conditions, ionisation occurs and a visible discharge is produced. The discharge is essentially a 'cold' plasma, in which the mean gas temperature does not usually increase much above ambient. The advantage of using microwave energy is that the plasma discharge can be made to fill the entire volume of a treatment chamber, rather than being restricted to a short spark as for a corona discharge.

Accordingly, experiments were carried out in which polythene strips were treated in a microwave discharge, then tested for autohesion in the manner described above. Specimens were treated in the plasma chamber of a large-volume microwave plasma generator (LMP). A photograph of a commercial version of the LMP is shown in Fig. 6. Details of this equipment have been published elsewhere,⁽²⁸⁾ but it is useful to point out certain important features. Instead of utilising a cavity resonator, waveguide or similar device, as did earlier microwave plasma equipment, the LMP employs a travelling wave structure as the means for applying microwave power to form the plasma. Consequently, whereas the former devices yielded maximum plasma volumes of the order of a few tens of cubic centimetres, plasma volumes of 1 litre or more can now readily be obtained with the LMP. Such conditions are approaching the requirements of industrial processing utilising microwave plasmas. Of further importance to the present work was the homogeneity of the LMP plasma, which assured uniform exposure to all parts of the samples.

Results are shown in Tables 4 and 5 for some initial experiments. Improvement in the bonding capacity was considerable in the case of cellulose strips treated in argon. Smaller but still definite increases were found for polythene. Some preliminary experiments were also carried out with an unbleached softwood kraft pulp. Treatment of the pulp as a dry fluff in the discharge increased

the breaking length by a factor of 2, but the sample used was unbeaten and therefore had a rather low breaking length to start with.



Fig. 6—Photograph of a commercial version of the large volume microwave plasma generator

(Courtesy of Compagnie de Physique Appliquée de Québec Ltée., COPAQ, Montreal)

TABLE 4—INCREASE IN THE WATER-INDUCED BONDING OF CELLULOSE STRIPS AFTER TREATMENT IN MICROWAVE DISCHARGE

<i>Gas</i>	<i>Pressure, torr</i>	<i>Time of treatment, s</i>	<i>Power, W</i>	<i>Bond strength, kg/cm²</i>
Control	—	—	—	1
Argon	45	120	100	113
Argon+5% oxygen	20	30	200	80
Air	20	120	200	16

It is interesting to note that the presence of oxygen is not necessary for the treatment to be effective in enhancing the bond strength. Both with cellulose strips (Table 4) and polythene strips (Table 5), an increase in bonding occurred after treatment in pure argon. This suggests that, as in the case of corona-induced autohesion of polythene, the enhancement of bonding is related to

the electrical characteristics of the discharge rather than to the chemical nature of the plasma gas.

TABLE 5—INCREASE IN THE AUTOHESION OF POLYTHYLENE STRIPS AFTER TREATMENT IN MICROWAVE DISCHARGE

Gas	Pressure, torr	Time of treatment, s	Power, kW	Bond strength, kg/cm ²
Control	—	—	—	0.9
Argon	75	5	1.5	1.6
Air	5	10	1.5	1.6
Argon + 5% oxygen	50	20	1.5	1.3
Helium	15	50	1.5	1.4
Helium + 5% oxygen	17	90	2.5	2.0

Adhesion of cellulose to synthetic polymers

SO FAR, we have considered only autohesion—that is, bonding between similar surfaces of the same material. Clearly, if combinations of cellulose materials and synthetic resins are to fulfill the promise currently seen for such composites, adhesion between cellulose and synthetic polymers is likely to become a crucial factor.⁽²⁾ Accordingly, it was of interest to investigate the conditions under which the thermally induced bond between various thermo-plastics could be increased by pretreatment of the surfaces in an electrical discharge. Strips of the cellulose and the polymer were treated in the corona; lap joints were made by pressing at various temperatures and the bond was broken in shear.

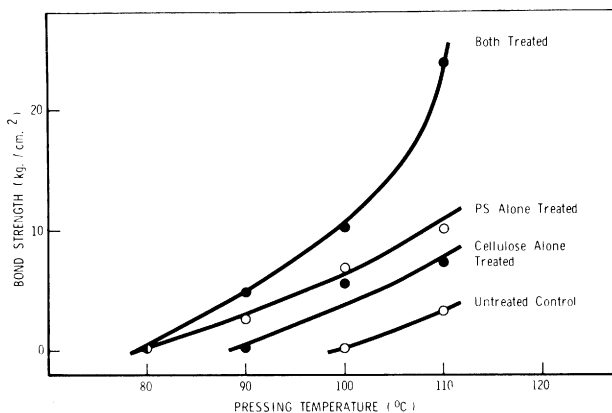


Fig. 7—Effect of pressing temperature on the bond strength between cellulose and polystyrene before and after corona treatment in oxygen gas

The change in bond strength plotted against the temperature of pressing for polystyrene and cellulose is shown in Fig. 7. Treatment was for 15 min in an oxygen corona (15 000 V and 60 Hz). The corona treatment not only lowers the temperature at which bonding begins, but produces stronger bonds at a given temperature. Considerable increase in bond strength was found when the treated polymer sheet was pressed to the untreated cellulose. A smaller improvement was noted when the cellulose alone was treated, but the bond strength shows the largest increase when both the cellulose and the plastic was treated in the discharge.

Results similar to those shown in Fig. 7 were obtained when a low density polythene, a polyvinyl chloride and a polyvinylidene chloride were bonded to cellulose. In all cases, the temperature at which adhesion became pronounced was below the softening temperature of the polymer.

The investigation was extended to the bond between thermoplastics and thin strips of wood veneer. In general, effects similar to those found with cellulose were noted. As shown in Fig. 8, treatment of the wood alone produced no significant increase in bonding. When the polymer sheet was treated, however, a marked improvement of bonding occurred and the maximum effect was found when both sheets were treated.

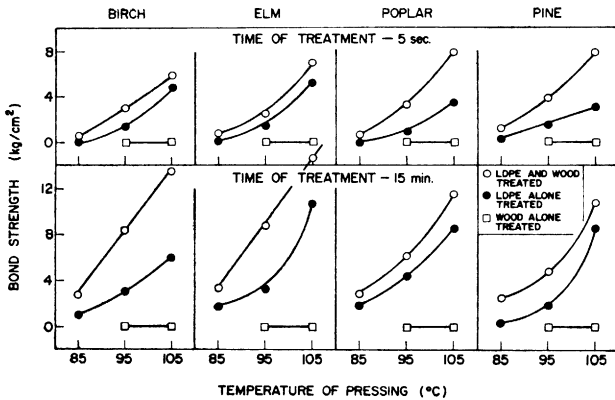


Fig. 8—Effect of corona treatment in air on the bonding between various woods and low density polythene (LDPE)

Surface roughness is often a factor in adhesion to wood. In the present work, it was found that sanding of the wood surface increased the strength of the bond. It was also noted that prolonged treatment in the corona discharge in air caused marked surface roughening of both the polymer and the wood. This is shown in Fig. 9 for polythene and elm. This effect may

have been a contributing factor to the decrease in bond strength found after long times of treatment. Significantly, treatment in pure nitrogen gas produced very strong adhesion in both cellulose/polymer and wood/polymer bonds, but no surface roughness could be detected even after long times of treatment in nitrogen.

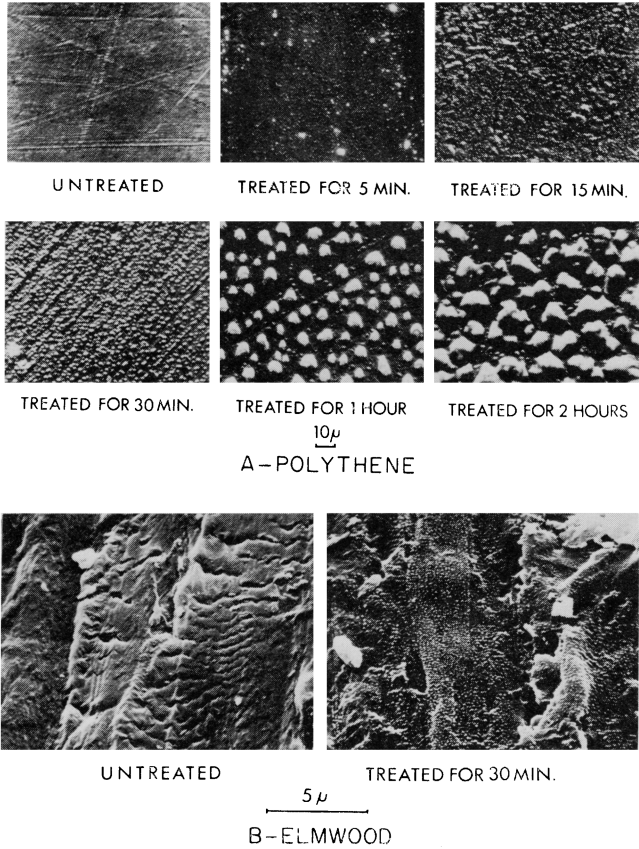


Fig. 9—Surface roughening of polythene and elm veneer after various times of treatment in a corona plasma in air

Using thin sheets of plastic, wood-polymer-wood laminates were made. In this case, corona treatment allowed bonds as strong as some plywood adhesive bonds to be formed. Results for birch and poplar, each laminated with high density polythene are shown in Fig. 10. No systematic study was

made of the effect of moisture on the permanence of the bond, but it was found that a birch-polythene-birch bond decreased from 40 to 15 kg/cm² after being soaked in water for 2 months at room temperature.

Composite hardboard

A MAJOR disadvantage of hardboards made from wood fibre is their tendency to absorb water from a humid atmosphere. Water uptake leads to swelling and dimensional instability and reduces the suitability of the product for exterior use. This is particularly true of hardboard made from poplar,⁽²⁹⁾ because of the relatively high hygroscopicity of poplar fibres compared with fibres from coniferous species.⁽³⁰⁾

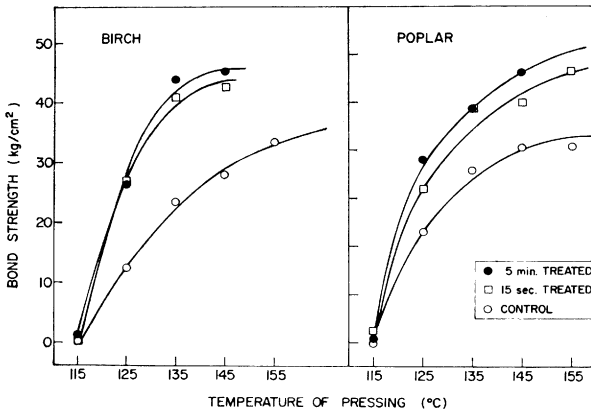


Fig. 10—Effect of corona treatment in air on the strength of laminates made by pressing a sheet of high density polythene between two sheets of wood veneer

Back and his co-workers have used both heat⁽³¹⁾ and chemical⁽³²⁾ treatments to enhance the dimensional stability of hardboards. In the present investigation, it was considered that, if a small proportion of an inexpensive thermoplastic polymer such as polythene could be incorporated into the board, the water resistance properties might be markedly improved. We therefore investigated the possibility of making a polythene/poplar fibre composite with improved water resistance, at the same time with strength comparable to the best quality boards available commercially.

By trial and error, it was discovered that the most suitable form for the polymer component was a fine powder. The fibre component was a pulp

produced by pressure refining of poplar wood. The air-dry fibre and the polymer powder were mixed mechanically and the required quantity of the mixture was pressed hot to give the finished board.

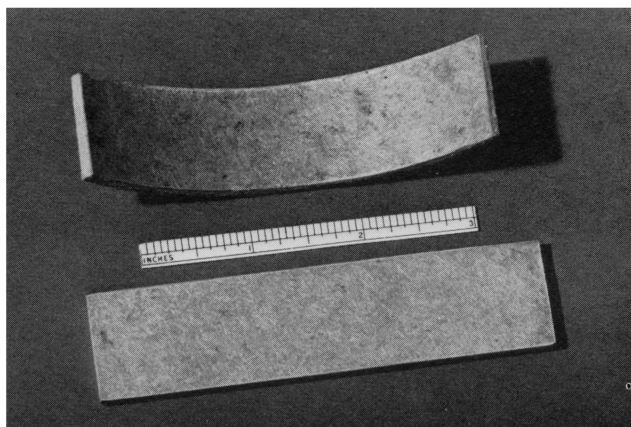


Fig. 11—Curved and flat specimens of composite hardboard

A photograph of a flat and a curved specimen of the composite hardboard is shown in Fig. 11. The curved specimen was made from a flat prepressed mat given the final hot pressing in a curved mould.

It is well known that the strength of a plastic/fibre composite depends on good adhesion between the fibre and the plastic component. We have seen that the adhesion between thermoplastics and cellulose or wood is greatly improved by pretreatment of the surfaces to be bonded in a corona plasma. Therefore, corona treatment of both the polythene and the wood fibre components of the composites was included in the experiments conducted.

As expected, corona treatment of the individual components produced a marked increase in the strength of the composite. A 5 min treatment of the polythene powder increased the rupture strength of the board by a factor of nearly two. Considerably smaller increases were observed when the wood fibre was treated.

Less expected was the marked effect of pretreatment in the corona on the water uptake of the composite. A 5 min treatment of the polythene powder before forming the board decreased the water uptake by a factor of two on submersion and nearly four on boiling. As in the case of strength increase, the most effective procedure was to treat the polymer powder. When the wood fibre was treated, the improvement in water resistance was much less.

A comparison of the performance of our best composite with two commercial hardboards is shown in Table 6. The strength and density of the composite are comparable with those of the commercial hardboard. The water uptake is slightly smaller and the water-induced expansions in width and thickness are, respectively, one third and one half those of the commercial boards. Thus, the polythene/wood fibre composite shows a substantially better dimensional stability than that found in the commercial board.

TABLE 6—COMPARISON OF THE PERFORMANCE OF POLYTHENE/WOOD COMPOSITE WITH TWO COMMERCIAL HARDBOARDS

Type	Density lb/ft ³	Modulus of rupture, lb/in ²	Submersion in water (24 h)			Boiling in water (1 h)		
			Sorp- tion, per cent	Increase in width, per cent	Increase in thick- ness, per cent	Sorp- tion, per cent	Increase in width, per cent	Increase in thick- ness, per cent
PE/Wood composite	68	9 000	16	0.17	9	23	0.11	19
Commercial-1	71	10 000	17	0.54	15	33	0.60	30
Commercial-2	67	8 000	23	0.47	20	53	0.75	41

One advantage of the present method over the conventional wetform process should be noted. Uniform formation of the web before pressing was not critical. Thermally induced flow of the low melt index polythene component allowed irregularities in the pad to be eliminated in the pressing operation. Moreover, because of the lower temperatures used, the original colour of the wood fibre is preserved in the finished board.

Concluding remarks

The present work has shown that the treatment of cellulose and polymer surfaces in corona or microwave plasmas can cause a considerable increase in the bondability of the surface. There is no need to stress the significance of these findings to the paper industry. One may ask several pertinent questions, however, about their application.

In what areas is application likely?

Somewhat nearer than the horizon is the use of synthetic polyolefin fibre as a component of pulp stock, using more or less conventional papermaking technology. Here, autohesion of the polymer fibres as well as cellulose/polymer adhesion will play an important role in the properties of the finished sheet. Perhaps the necessary surface-conditioning of these new fibres will become a technological route to the application of plasmas in the paper industry.

It also seems likely that new composite materials with improved properties will be competing with hardboard, particleboard, perhaps even paperboards. Here too, polymer/cellulose bonding will be of crucial importance and pre-treatments may be required to ensure the development of appropriate surface properties.

What about costs?

Compared with other forms of radiative treatment, corona and microwave processing are relatively inexpensive. Coffman & Browne⁽¹³⁾ estimate that corona energy can be delivered to the reaction site at 1–3 cents/kWh. The cost of microwave plasma application is likely to be about the same. This may be compared with 35 cents/kWh or more for high energy beams.⁽¹³⁾

A further point to note is that the plasma reacts only with the surface. Therefore, in a properly designed process, the quantity of material treated per unit of energy applied is apt to be high.

What about the environment?

Here, of course, prediction is extremely difficult until more is known about the details of any proposed process. In both paper and board making, however, liquid effluent problems beset our current technology. If cellulose/polymer composites lend themselves to dry-forming techniques, some liquid effluents would be eliminated, thereby improving the environmental performance of our mills.

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References

1. Young, J. R., *Paper Packs*, 1966, Dec., 23–37
2. Noll, P. B. and McAllister, J. E., *Paper Film Foil Conv.*, 1963, Oct., 46–49
3. Rossman, K., *J. Polym. Sci.*, 1956, **19**, 141–144
4. Greene, R. E., *Tappi*, 1965, **48** (9), 80A–84A
5. Goring, D. A. I., *Pulp & Paper Mag. Can.*, 1967, **68** (8), T372–T376
6. Goring, D. A. I. and Suranyi, G., *Pulp & Paper Mag. Can.*, 1969, **70** (20), T390–T397
7. Kim, C. Y., Suranyi, G. and Goring, D. A. I., *J. Polym. Sci.*, 1970, **C30**, 533–542
8. Kim, C. Y. and Goring, D. A. I., *Pulp & Paper Mag. Can.*, 1971, **72** (11), T363–T366
9. Kim, C. Y. and Goring, D. A. I., *J. appl. Polym. Sci.*, 1971, **15**, 1 357–1 364
10. Kim, C. Y., Evans, J. and Goring, D. A. I., *J. appl. Polym. Sci.*, 1971, **15**, 1 365–1 375

11. Wertheimer, M. R., Suranyi, G. and Goring, D. A. I., *Tappi*, 1972, **55** (12), 1 707
12. Brown, P. F. and Swanson, J. W., *Tappi*, 1971, **54** (12), 2 012–2 018
13. Coffman, J. A. and Browne, W. R., *Scientific American*, 1965, **212** (6), 90–97
14. Bogaty, H., Campbell, K. S. and Appel, W. D., *Textile Res. J.*, 1952, **22**, 81–83
15. Samuelson, O., Grangard, G., Jönsson, K. and Schramm, K., *Svensk Papperstidn.*, 1953, **56** (20), 779–784
16. Schuerch, C., *J. Polym. Sci.*, 1963, **C2**, 79–95
17. Liebergott, N., *Pulp & Paper Mag. Can.*, 1972, **73** (9), T214–T217
18. Soteland, N. and Kringstad, K., *Norsk Skogind.*, 1968, **22** (2), 46–52
19. Voyutskii, S. S., *Adhesives Age*, 1962, April, 30–36
20. Bockhoff, F. J., McDonel, E. T. and Rutzler, J. E., *Ing. Eng. Chem.*, 1958, **50**, 904–907
21. Sykes, J. M. and Hoar, T. P., *J. Polym. Sci.*, A–1, 1969, **7**, 1 385–1 391
22. Stradal, M. and Goring, D. A. I., to be published
23. Hansen, R. H. and Schonhorn, H., *J. Polym. Sci.*, 1966, **B-4**, 203–209
24. Schonhorn, H. and Hansen, R. H., *J. appl. Polym. Sci.*, 1967, **11**, 1 461–1 474
25. Gross, B., *Phys. Rev.*, 1944, **66**, 26–28
26. Perlman, M. M. and Meunier, J. L., *J. appl. Phys.*, 1965, **36**, 420–427
27. Sessler, G. M. and West, J. E., *J. Electrochem. Soc.*, 1968, **115**, 836–841
28. Bosisio, R. G., Weissflock, C. F. and Wertheimer, M. R., *J. Microwave Power*, 1972, **7**, 325–346
29. Sinclair, G. D. and Dymond, D. K., *Tappi*, 1968, **51** (9), 108A–111A
30. Ahlgren, P., Wood, J. R. and Goring, D. A. I., *Wood Science and Technology*, 1972, **6**, 81–84
31. Back, E. L. and Klinga, L. O., *Svensk Papperstidn.*, 1963, **66** (19), 745–753
32. Klinga, L. O., Tarkow, H. and Back, E. L., *Svensk Papperstidn.*, 1965, **68** (17), 583–587

Transcription of Discussion

Discussion

Dr E. L. Back One of the things that David Goring pointed out to us today was that water was not necessarily a bonding agent for cellulose fibres. I would like to extend this into one other area of high energy bonding in which David Goring has done much fundamental work. He was the first to point out years ago that cellulose has a glass transition, which I think we all agree now is about 230° C. It is reasonable that as for all other plastics above this glass transition temperature, somewhere around 300° C, it would be possible to bond cellulose in the absence of water. Some years ago, we examined the heat ceiling of water-free cellulose, which was shown to be possible in this range. Recently, we made a few experiments producing paper sheets completely water-free. The sheets were preformed in benzene and bonded together by heat at about 300° C to give reasonable strength properties.

We calculated earlier the melting point of cellulose from its glass transition temperature as $450^{\circ} \pm 15^{\circ}$ C. It is possible to use this for bonding as well as for decreasing the crystallinity of cellulose. Naturally, this quenching to above the melting point and down again has to take place very rapidly (within about a micro-second or less) to prevent breakdown. We have tried this in a high energy laser beam. A paper sample mounted on a revolving holder after passing the laser beam goes immediately into liquid nitrogen. The illustration (Fig. A) shows a scanning electron microscope picture around the hole shot by the laser beam. To the left, away from the hole in the upper right corner the fibril structure of this highly beaten kraft paper is intact. Near the hole, the fibril structure disappears, we have a formation of small bubbles, probably caused by water of dehydration formed in the melt. On collected material of this type, the crystallinity has been determined by infra-red indices. In this case, the crystalline part of the material has gone down from 65 per cent to 30 per cent.

Looking into the future, beyond the year 2000, it might be possible to visualise the melt spilling of cellulose fibres in a laser. The important point is the possibility of bonding paper in water-free conditions.

Under the chairmanship of Dr H. Corte

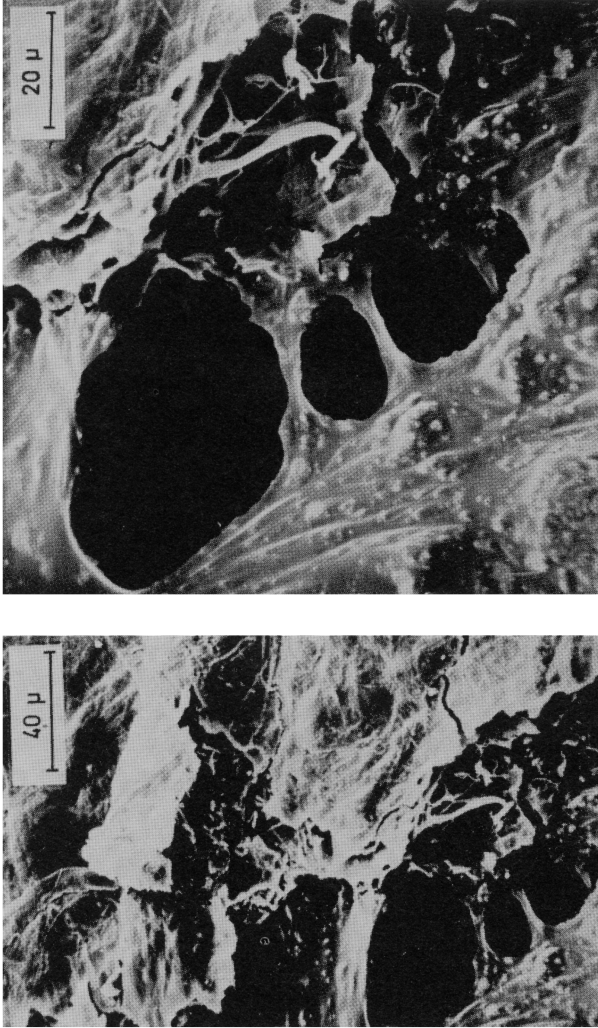


Fig. A—Scanning electron microscope picture at hole shot into a highly beaten kraft paper by a laser beam: near the hole the material has lost its fibril structure and bubbles occur

Dr P. Luner You proceeded, Dr Goring, from discussing cellulose-to-cellulose bonds to cellulose-polymer bonds and towards the end of your discussion the explanation you invoked for the increase in adhesion was the use of electrets. This might seem reasonable for the cellulose-polymer and polymer-polymer interactions, but is this the explanation for the cellulose-to-cellulose bonds as well?

Dr D. A. I. Goring We found evidence of electrets on some cellulose sheets, for instance, on regenerated cellulose film. We think, however, that the burden of the work of the discharge on cellulose is to oxidise it and produce a layer that swells and bonds. This is because much the same effect is obtained by treating the cellulose with the gases effluent from the corona. There is another great difference. The autohesion in polymers is primed by treatments of a fraction of a second, but to prime cellulose with a corona a longer time is needed, which suggests that oxidation is indeed playing a part. I think that the electret phenomenon is particularly important in the autohesion of polymers, that is, in the sticking of polythene to itself.

Dr Back's contribution is an interesting, but far-out concept. If you heat a mass of cellulose by conventional means to make it bond, you will destroy the cellulose and its structure. There are two ways out of this. One is to devise means of heating it very quickly, bonding it, then cooling it down very quickly, because (as I mentioned, maybe not in this room, but certainly at this meeting eight years ago) chemical reaction rates increase by a factor of two every 10° C, whereas the viscoelastic properties of the polymer near its softening temperature change by a factor of 1 000.

Another possibility is, by application of some kind of highly localised energy, to heat up only 100 Å or so of the surface of the fibre. Thus, if you could form the sheet and cause this effect to occur only at the bonded areas, you could heat seal the bonds and not alter the basic strength properties of the sheet.

Mr A. Brucato In your initial comments, you said that you had considered all the various mechanisms that might be responsible for the adhesion that is taking place, but would not go into them at the moment. I was just wondering if one of these may have been the creation of free radicals on the surface of the material involved, since with polythene and cellulose polymers subjected to these conditions, you may be producing a skin containing free radicals, which can then act with the surrounding air or oxygen or, if nitrogen is in the environment, then the free radicals remain until they have an opportunity to react with something.

You also commented that these effects are time-dependent, which suggests

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also the decaying of free radicals. It seems to me that the bonding being a consequence of free radicals generated on the surface has a very strong possibility and the material so treated could be analysed for the presence of free radicals. Has this been pursued?

Dr Goring What method of analysis would you suggest? I had two postdoctorals and two students on this project and three of these each in turn made it their main vocation in life for about six months to demonstrate a free radical mechanism. They exhaustively studied the effect by electron spin resonance to try and spot free radicals. You will of course produce free radicals when you treat the surface in oxygen, but in treating it in the non-oxidising gases like nitrogen, helium and argon we have failed to detect free radicals. We have also taken the corona-treated surface and put all sorts of free radical quenchers on this. If the bonding depended on free radicals, you would expect that the free radical quenchers would stop the bonding, but they don't. We therefore moved away reluctantly from the free radical hypothesis.

Mr Brucato With the time-dependency of adhesion, would temperature conditions influence the ability to bond as might be the case if there were free radicals that might decay more rapidly if they were heated?

Dr Goring Yes, very definitely. As you take the temperature up, the ability to bond decreases more rapidly with time. Of course, as you take the temperature up, the electrets disappear more rapidly with time, too. In fact, an electret is really a kind of free radical, isn't it? If you just for a moment forget your chemistry, what you have done is to embed electrons in the surface of the polymer. The electrons are not localised, which means that they are not associated specially with any part of the polymer chain. Nonetheless, they are free electrons in the surface of the polymer, so that the electret is indeed a kind of free radical.

Mr V. Wolpert Have you made any experiments of bonding polypropylene, which of course has on one hand a higher melting temperature, about 20° difference, but on the other hand has the possible advantage of a lower specific weight than polythene.

Dr Goring We have tried experiments with polypropylene and you can get these effects, but they are not as pronounced or as strong as we found in the case of polythene. Milos Stradal has also recently done experiments with polythenes of varying density. The results show that the effect is graded and that the higher the density of the polymer, the less effectual is the corona treatment

in improving the adhesion—it works best with a low density material. I think the reason for this is that, with a high density material, it is more difficult to produce a high free volume layer on the surface of the polymer, because the crystalline structure interferes.

Dr J. Marton You mentioned that the increased adhesion between cellulose surfaces was associated with or was caused by the formation of carboxyl groups during the ozone treatment. I wonder did you study the effect of trace metals on this type of surface modification. Transition metals may affect the formation of carboxyl or carbonyl groups, whichever is the more desirable. Judicious application of chosen trace metal catalysts may influence or increase the desired adhesion effect. This is pretreatment with transition metal catalysts.

Dr Goring No, we didn't try this, but it would be interesting. You could correlate the increase in oxidation (measured with infra-red) with the increase in bonding.

Dr E. Graminski A free radical mechanism could explain the difference in polythene bonding after corona treatment in air, nitrogen and ozone. In air, some free radicals recombine while some react with oxygen, resulting in a decrease in molecular weight at the surface. The softening temperature would decrease and bonding would occur at lower than normal temperatures. In nitrogen, the free radicals would only recombine, while in ozone a large number of polar groups would be produced at the surface, resulting in an increase in hydrophilic character. In neither case could we expect an improvement in bonding at lower temperatures. This point could be verified by measuring the surface energy of the polythene before and after treatment. Has this been done? Did you also measure the contact angle?

Dr Goring Yes, we have done this and we find that the contact angle in the ozone treatment and in the corona treatment both changed as you would expect from increased oxidation—you get increased hydrophilicity, as you say. We have also found that the molecular weight in oxidation does decrease. Oxidation degrades the surface, in fact, we get spectacular physical effects. The illustration (Fig. B) shows what happens to a polythene surface treated for longish times at increasing temperatures. The surface characteristics have been changed rather drastically. As treatment proceeds, bumps develop on the surface that seem to coalesce into bigger bumps with prolonged time of treatment. Interestingly, you can wash the bumps off with an alcoholic or aqueous alkali. What we think is that the ozone in the corona is degrading

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the surface and electrical field effects are attracting the degraded material somehow or other to paths of least electrical resistance in the polymer, so bumps of low molecular weight material grow that can quite easily be removed. What you must understand is that the bumps occur at times of treatment that are very much longer than the times required to effect adhesion (that is, in minutes), whereas strong adhesion arises by treating a surface for a fraction of a second, in which time no detectable changes in surface characteristics take place.

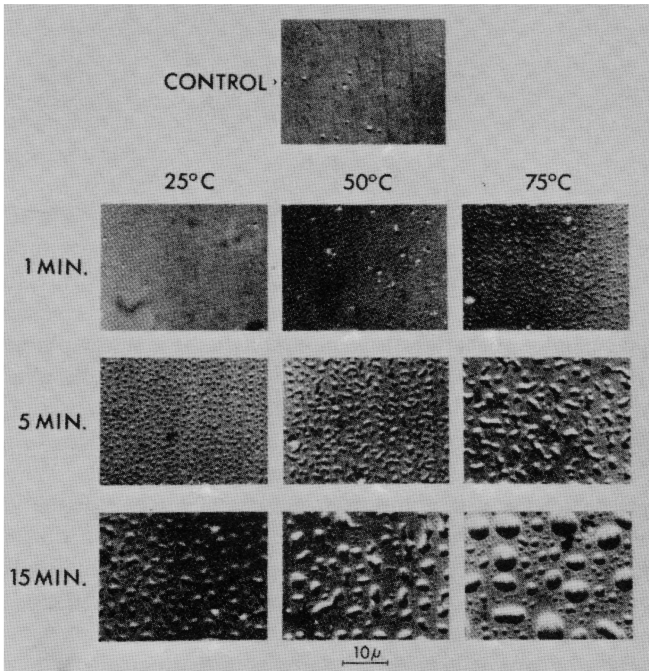


Fig. B

Another point is shown in the next illustration (Fig. C). Here, the bumps produced by treatment in air are shown alongside the surface treated in nitrogen. We could detect no physical difference in the surface even after very long times of treatment in nitrogen. This suggests that the ozonised oxygen is degrading the surface and producing the bumps, but it also suggests that surface degradation as such is not necessary for autohesion, because perfectly good adhesion is obtained in nitrogen—in fact, even stronger than in oxygen.

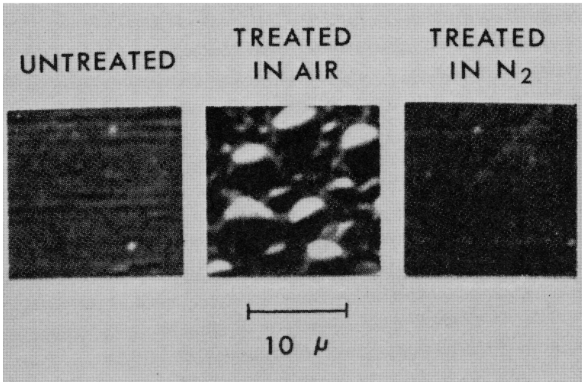


Fig. C

Mr J. S. Harris You mentioned that the bonding strength between cellulose and cellulose rose by several times, but that the tensile strength remained the same. Could you say why you thought this was so?

Dr Goring This was the tensile strength of the strip that we were bonding. Now, the treatment of cellulose in the corona was done in the dry state. We know that gases penetrate very little into cellulose in the dry state. Therefore, the ozone would degrade only the surface and would not enter into the bulk of the cellulose and weaken the tensile strength of the strip. When treating fibres, this is of course something that one would have to watch. We found, for example, that if the strips were damp and were treated for a long time in the corona, they became fairly weak; you could reduce their tensile strength by a factor of ten. Under the conditions of treatment used here, the tensile strength was only very slightly reduced, because the reaction was restricted to a thin layer on the surface of the material.

Mr Back I would like to repeat a question I asked a couple of years ago—to what extent are covalent bonds formed in the corona treatment? To what extent do you produce wet strengths in this bonding?

Dr Goring I can only answer this question by referring to a result that we found surprising. When making the boards, we expected to get increased strength, but we never really expected to get increased dimensional stability, because the corona treatment was done not in nitrogen, but in air and one would expect increased water uptake arising from the oxidation. In fact, we

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obtained increased dimensional stability. Whether or not this is due to some type of covalent bonding I do not know, but we have no direct evidence for covalent bonds.

Dr J. A. Van den Akker Mr Radvan referred to Rupert Maynard's discovery some years ago that paper has a negative Poisson ratio. This is of course tremendously intriguing to everyone interested in paper structure. One of our students at the Institute of Paper Chemistry, I. B. Sanborn, studied the effect of tensile loading on the structure of paper, with special reference to permeability. I believe it was in that study—I will have to check on this—that he carefully measured the thickness of a paper specimen as a function of load and found that at small strains the Poisson ratio was positive (the thickness decreased). Then, as the load was increased, the thickness returned to its initial value and began to increase—in other words, the Poisson ratio became negative at larger strains.

Dr J. Mardon Illustrations show typical drainage profiles on four different two-wire formers and how different they can be. There are three different patterns, two are essentially the same and these are quite characteristic of the different formers. The loading distribution is very similar to that shown for fines. Other illustrations show a typical cross-direction section of one of the two-wire formers and one has these particularly little nodes in it scattered through the sheet, which are quite characteristic and illustrate the kind of thing that differentiates one type from the other in the paper structure.

Dr J. Grant Speaking in general terms, I gather that you are really in agreement with me in that the two-wire machines produce a more uniform distribution of loading throughout the cross-section of the sheet. This is the point I am trying to make, because I think I remember you saying that the Fourdrinier machine gives better papers. I am disputing that particular epithet, because the distribution of loading evenly throughout the cross-section is extremely important nowadays, because of the increasing use of newsprint for web offset printing.

Mr Radvan When you made these composite boards by the dry method and saw better adhesion, you also mentioned, Dr Goring, that in another context the autohesion of plastics could stand the presence of quenching agents, free radical quenchers. Would it also withstand water?

Dr Goring Yes, it withstands water. That is, you can bond them wet and still get the increased adhesion. Incidentally, the charge does not withstand

water. If you wet the sheet, you discharge the electret. This is why I say that the bonding is not electrostatic. Something is left in the surface that is not an electric charge and that promotes adhesion even when wet.

Dr N. K. Bridge Have you ever found any effect worth noticing of your electrical discharges on the optical properties of cellulose materials?

Dr Goring We never looked carefully for this with our cellulose materials. I am trying to remember whether we ever saw on the various cellulose films we treated any sort of clouding of the surface owing to the corona treatment. Certainly, on long treatment, we should have observed some clouding, because the surface is roughened. With the polythene, there is indeed quite a marked optical effect. A transparent sheet of polythene will develop something of a sheen on it, which makes it slightly opaque. Again, the length of treatment to produce these effects, particularly in the case of synthetic polymers, is far greater than is required to produce adhesion.

Prof. D. Wahren Have you tried any other methods of making electrets out of paper. I want to refer to experiments by Dr Kubát many years ago, in which he made electrets out of paper by subjecting the paper samples to slightly elevated temperature, sometimes also to moisture in combination with an electrical field. He found electret effects, but (so far as I know) he never tried to combine several pieces of paper after the treatment.

Dr Goring No, we have not attempted this. One experiment we should do some time (if we can find someone who will let us do it) is to use a source of high energy electrons and see if these will also produce electrets in the polymer surface, but we have not looked at other means of creating electrets.

Mr A. de Ruvo You mentioned the adhesion theory of Voyutskii, which I think gives a very clear picture of what happens during adhesion—it is a matter of solubility between the two faces. Of course, with solubility, one also starts to think about precipitation. An interesting aspect with two cellulose surfaces coming together in the amorphous state would be a precipitation leading to crystallites between the fibres, thus giving a tighter bond, which would be water resistant. Can you think of any experiments that would indicate that such bonds can really be formed between two cellulose fibres?

Dr Goring Yes, I could think of experiments, but they have nothing to do with corona. If you treat a sheet of paper with nitrogen dioxide gas, it looks no different, but the wet strength is about equal to the dry strength. What has

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happened is that the gas has decrystallised the cellulose. When the gas is exhausted, the cellulose recrystallises and crystalline bonds are formed. Paper treated in this way is just about as strong as the original sheet. It suffers a slight loss in brightness, I think. It is much more brittle and its wet strength is a high proportion of its dry strength.

Your comment gives me another thought. Polythene is a crystallised polymer. The corona treatment creates a high volume, amorphous layer on the surface. Perhaps in addition to Voyutskii type interdiffusion, some recrystallisation occurs in the layer between the two sheets, which could enhance adhesion.

Dr Grant None of the theories put forward to explain the phenomenon that Dr Goring has described mentions the manufacture of vulcanised fibre, which (it seems to me) does precisely what his process does. It enables laminae of cellulose to self-adhere very firmly, it produces high wet strength and it produces dimensional stability. Is there any analogy between the effect of sulphuric acid or zinc chloride on the surface of the fibre and your corona?

Nobody really knows, of course, what the action of the sulphuric acid is, but we know that it does just the same thing as the corona. It is basically the process for making vegetable parchment, of course. In making vulcanised fibre, one makes two parchmentised layers and laminates them (so to speak) by bringing them together. The same effect is obtainable with zinc chloride solution.

The sulphuric acid does not penetrate the fibre and its action has to be very carefully controlled. I am not disparaging the academic importance of your discovery.

Dr Goring Although we did not try the parchmentising reaction, we tried many other chemical treatments of cellulose and none of them worked as well as the corona treatment in increasing adhesion. The other point is that, although several kinds of strong chemical treatment of a polythene sheet are known to increase its adhesion, such methods are not in commercial use so far as I know. Yet corona treatment is widely used for the treatment of polythene sheet.

Dr H. Minshall May I ask Dr Moffatt whether he has done any work on supercalendered newsprint as distinct from the machine-calendered newsprint he was talking about this morning?

Dr J. M. Moffatt I think this may be a good time to come back to explain the field of this problem a little and return to the points raised by Dr Lyne

also, with his experience of finding a break-line in regular newsprint that did not go through the high grammage points. One could make a number of superficial points here: is the type of newsprint exactly the same, is the mode of calendering the same, there is a difference in rupturing methods, etc. What would be a most important point though, to answer Dr Lyne, would be to know what his grammage distribution in the break zone actually was compared with that for uncalendered paper.

The calender damage that I was talking about in my presentation occurs when the density of high grammage points exceeds a critical density, as can occur notably on hard calendering. We have reason to believe that this critical density is that of wood substance. One gets a very rough check on this by extrapolation. You can show that the highest grammage in the population of the uncalendered newsprint used when divided by the caliper at which the strength starts to fall off gives a critical density that is identical with that of wood substance. This is a subject, however, that could be usefully studied further.

Now, any precompression action such as breaker stacks and wet pressing will smooth down the sheet before it gets to the calender stack, hence will attenuate the weakening effect we noted, also the fact that the break-line grammage distribution increases with calendering. You will also get various consolidation effects and better bonding. The soft calender if used will result in not exceeding the critical density or it becomes increasingly unlikely that you will exceed the critical density, because in this case it will be the material in the calender that yields instead of the material of the sheet. In one of two small experiments on the effect of soft calendering, the grammage distribution in the break-line was little higher than that of uncalendered paper, but it was still below that of the random samples taken. I think that answers your question, also some of the other points earlier this morning.

The Chairman I would like to comment on one point in Prof. Wahren's contribution—his result that paper is more uniform than random on a small scale. If this is so, how much more uniform would it be on a large scale! For larger areas (for example, A4 sheets), the variance of the random grammage distribution is given by a simple formula—

$$\text{Var}(\text{grammage}) = \lambda w W / a,$$

where the area of inspection a is 625 cm², λ is the mean fibre length, w is the mean weight per unit length of the fibres and W is the mean grammage of the sheet. The square root is the standard deviation and, when this is multiplied by three, it gives the grammage range in which 99.73 per cent of all A4 sheets should lie. For a 100 g/m² sheet of paper and typical values for the fibre

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dimensions, the result is a range of about ± 0.05 per cent, which is well below the accuracy of technical measurements of weights and areas. If you produce a ream of A4 sheets with that sort of standard deviation of their grammages, then I believe you.

Mr S. Punton Prof. Wahren, you referred to Wrist's suggestion (1961) that during sheet drainage thin spots are filled owing to increased flow in those areas. You also say that there was no theoretical or experimental evidence in 1961 to support this. Is there any direct evidence available today?

Prof. Wahren Quite a few experiments of this kind have been carried out. Parker did some fine experiments and the results were published in *Tappi*. He put a tape across the wire of a handsheet former. He could then show that, in fast drainage, the fibres could move sideways quite appreciably. In slow drainage, a thin sheet was formed on top of the tape. Wrist suggested a method in 1961 by trying to draw a random sheet with a computer. At that time, computer technology was not advanced enough for him to succeed quantitatively. We repeated this experiment and we also have a mathematical model of a random sheet. We can compare the theoretical results with the practical results.