

SURFACE CHARACTERIZATION OF COMMUNICATION PAPERS

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ABSTRACT

The characterization of surface properties of communication papers reflects both handling and printing requirements. Test methods recently applied in this area range from simple adhesive strength characterization and liquid penetration tests to more sophisticated gas chromatographic and spectroscopic procedures suitable for thermodynamic and chemical constituent analysis. The principles and results of such testing are reviewed.

INTRODUCTION

Communication papers, that is, papers used for input to, or print-outs from computers, systems printers, copiers, laser printers, and other similar printing and writing devices, have received more attention from the paper maker as these printer types have proliferated during recent years. The xerographic or 'copy' paper grade now accounts for a large fraction of the papers that are not only used for non-impact copying and printing, but also for other applications in the office and systems printing environment. This variety in usage and the technology of different printing procedures put specific demands on both handling and print quality of these papers. The surface characteristics, both physical and chemi-

cal, are key parameters to be adjusted accurately for the intended applications. This has required the application of a range of both simple and more sophisticated analytical techniques for paper surface analysis, other than those that generally have been used for development and quality control in the mill environment.

The use of novel surface characterization techniques for the analysis of papers used in non-impact printing has been motivated by two reasons. Firstly, with the development of fast-speed high volume printers, it is often not possible to carry out the 'trial-error' printing typical of paper development for slower-speed printers and copiers. Secondly, there is a requirement to develop multi-purpose paper brands suitable for a number of specific printers not necessarily applying the same printing technology. This requires a better fundamental understanding of the imaging and handling processes in terms of needed paper characteristics. At the same time, the switch-over to alkaline papermaking has required a more extensive analytical support than merely an adjustment of traditional paper characteristics to new requirements.

This paper reviews some of the techniques that have been or could be moved from the cellulose and paper research environment to the paper development and quality control stages.

PAPER NATURE

Communication papers may be divided into two groups: plain or specialty grades. The latter, which is specifically adjusted for the printing machine in question, will not be considered in this review. Plain grades are generally uncoated papers of much lower cost and higher volume than the coated or otherwise specifically treated specialty grades.

In the U.S., the 'plain', yet 'not so plain', bond paper has evolved into the xerographic paper grade. Originally, this was a somewhat smoother

bond-type paper of controlled humidity and curl characteristics. Lately, multi-system paper types have become available. These are often more heavily modified papers, where the paper chemistry has been affected through modification of the amount and nature of size and filler.

Specific surface treatments may be carried out on the size press without the added cost of specific coating procedures (1). This makes the changes invisible to the end user and to the paper technologist alike. The latter, however, will require more effective means of characterizing changes in surface chemistry. The concept of surface energetics and other characterization parameters obtained using gas chromatographic and spectroscopic analysis techniques are gaining increased usage.

SURFACE TOPOGRAPHY

Recent trends towards smoother papers are motivated by the desire for better print quality. For example, several desktop laser printers now print at a resolution of 600 dpi. Print quality variations due to surface smoothness are particularly pronounced for equipment using hard roll fixing (2,3). Other imaging techniques using molten inks, such as thermal transfer printing, suffer from similar limitations (4,5) (Fig. 1).

While other methods have been suggested for surface topography analysis of communication papers (1), air leak characterization of surface smoothness is often preferred. ASTM D 3460 (6) contains the specification ranges shown in Table 1. The range shift for xerographic and laser printer papers from that of general bond paper is due to the requirements of newer copier and printer designs including those intended for color imaging. Although rougher paper is better tolerated in higher speed systems printers where print quality demands are less exacting, also these machines now require the consideration of surface smoothness characteristics (7).

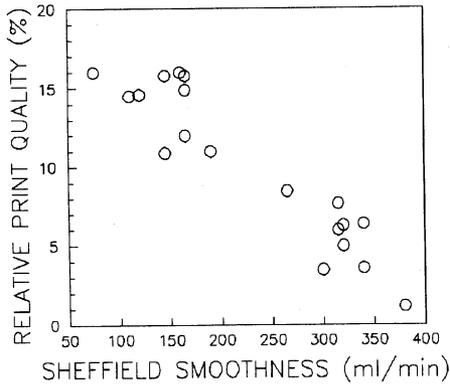
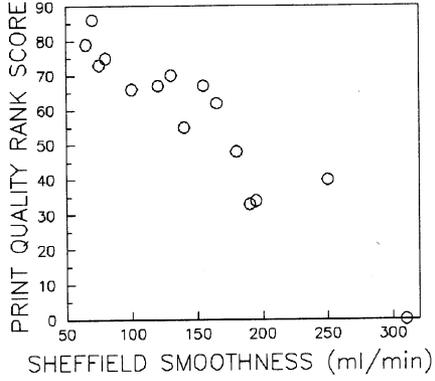


Fig 1-Examples of the effect of surface smoothness on print quality in thermal transfer printing (from refs. 4 and 5).

Paper type	Smoothness range (Sheffield)
Bond	235 to 100 units
Mimeo	340 to 200 "
Spirit duplicator	100 to 65 "
Xerographic	200 to 65 "
Laser printer	200 to 65 "

Table 1. Smoothness ranges for cut-sized office papers (from ref. 6).

The processing of very smooth papers (<100 Sheffield units) requires a paper path where paper handling is not impeded. The problem areas are those where contact occurs between paper surfaces or the paper surface and other surfaces during processing. Pending the deformation characteristics in the contact area (see Friction and Adhesion, in the following), adequate paper handling may not be achievable. Additional electrostatic forces in photoconductor contact or in contact with other smooth machine parts, will further aggravate this situation (2).

FRICION AND ADHESION

Paper-paper friction testing of communication papers is generally carried out using the horizontal plane method (8). Testers based on this principle are commercially available for testing sheet materials. The measurement of friction between paper and other machine components (for example, paper feeding belts) may require special fixtures (9).

While friction testing often is included routinely among required test procedures for communication papers, there has been less research carried out in this area than in other fields of paper physics. Much literature data is of a descriptive nature, and only recently has a comprehensive review of paper friction been presented (10).

The friction coefficient μ between paper and a counter surface may be described by the following components (11):

$$\mu = F/L = \mu_{ad} + \mu_{ab} + \mu_h \tag{1}$$

where F is the friction force, L is the normal load, and μ_{ad} , μ_{ab} and μ_h are contributions due to adhesion, abrasion and hysteresis, respectively. For most applications handling single sheets of paper, only moderately normal loads are involved, and conditions of abrasion and hysteresis will not be created. Friction is mainly of an adhesive nature where the friction coefficient is constant since the friction force will vary linearly proportional to the load (Amonton's second law).

In practice, this means that the paper-paper and paper-metal friction coefficients are relatively unaffected by paper smoothness or metal surface roughness (10,12) but may vary considerably due to chemical factors (for example, extractive content or filler content and nature) (10) (Fig. 2).

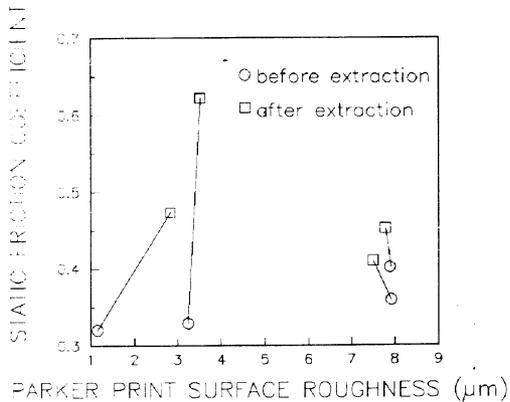


Fig 2-Paper-paper static friction coefficient of different papers of varying surface roughness before and after solvent extraction (from ref. 10).

In contrast, the paper-rubber friction coefficient will vary exponentially with normal load (9):

$$\mu = CL^{-N} \quad (2)$$

where C and N are interrelated as shown in Fig. 3. This imposes different friction levels for paper-rubber friction, an increase in friction coefficient for smoother papers, and a friction action that much more easily degrade the paper surface (13) (Fig. 4).

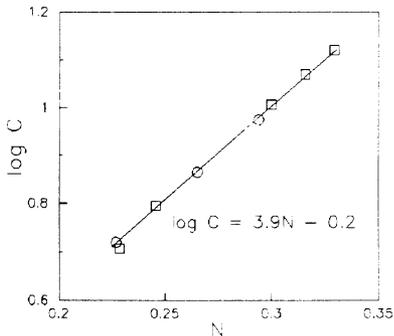


Fig 3-The relationship between C and N for silicone rubbers (from ref. 9).

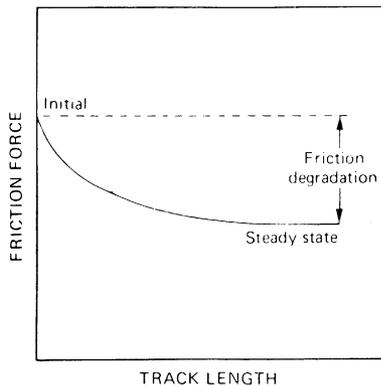


Fig 4-Friction degradation for paper-rubber friction (from ref. 13).

The paper-paper friction coefficient, as required by most cut-sheet copiers and printers, ranges from 0.35 to 0.7. This is indeed the general range found for most bond type papers without any specific surface treatments. However, the friction characteristics during initial sheet separation may be critical to good functionality. Generally, the initial or static friction level is required to be larger than friction during subsequent sliding (kinetic friction). This may be compromised for synthetic sized papers of excessive synthetic surface size content (14) (Fig. 5).

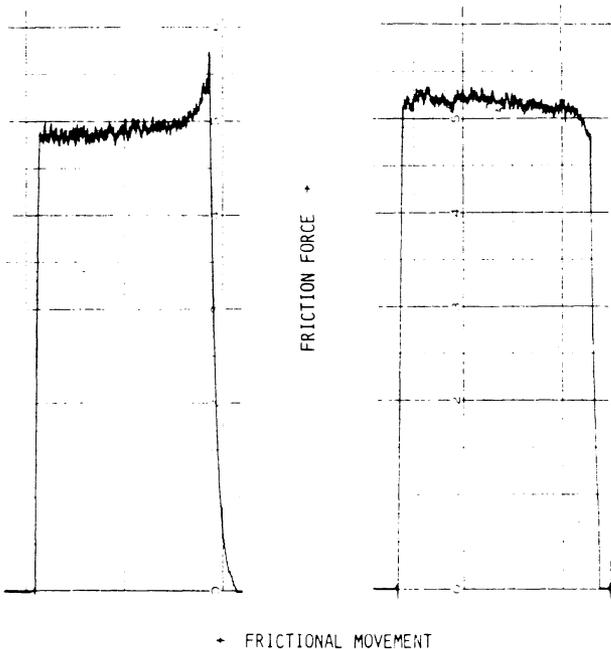


Fig 5-Paper-paper friction trace of a synthetic sized paper type (right) compared to that of a rosin sized paper type (left) (from ref. 14).

The role of surface filler content in paper friction variation is still not completely clear (15) (Fig. 6). Recently, oil absorption levels have been correlated with paper-paper friction levels for sheets containing synthetic precipitated silica and silicate pigments (15) (Fig. 7). This suggests that the same surface chemical factors, that are effective in increasing friction for the solvent extracted sheets in Fig. 2, are effective here. That is, fatty acids and other friction decreasing constituents are no longer present on the surface.

The thermodynamic nature of paper adhesion has recently been reviewed (16). Paper-polymer adhesion plays a critical role for communication papers that are imaged with toners or other polymeric films or particles. Specific test procedures and devices have been developed for specific types of print (17), but often simple joint peel testing will reveal the adhesive nature of the paper surface itself. Relatively simple experimental procedures can quantify variations in 'practical' adhesion when specific tape types are used for laboratory testing (18).

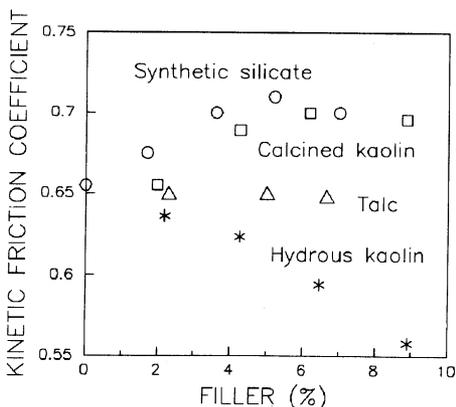


Fig 6-The effect of different filler types on the paper-paper kinetic friction coefficient (from ref. 15).

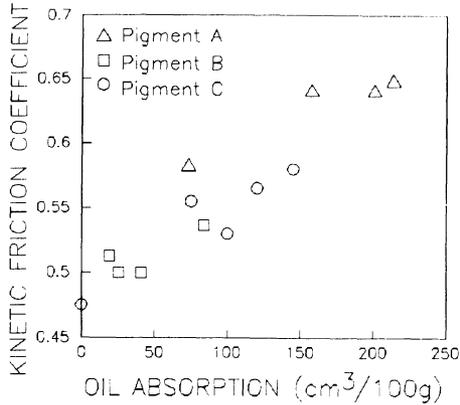


Fig 7-The effect of oil absorption of different pigments on the paper-paper kinetic friction coefficient (from ref. 15).

The failure mode of adhesive tape removed from plain paper has been characterized as 'interface failure', 'mixed failure' or 'paper failure' (19). This is well-known by paper technologists who often use tape to split commercially-made sheets into individual layers. For interfacial failure (Figs. 8 and 9), the tape will release cleanly from the paper surface since tape-paper adhesion is insufficient to generate failure in the paper fiber matrix. As seen in Figs. 8 and 9, the peeling force increases with peeling rate possibly reflecting the viscoelastic properties of the tape adhesive. The paper failure mode generated in the sheets of low bonding strength (cohesive failure for less mechanical refining in Fig. 8 and for filter paper in Fig. 9) reflects the cohesive strength of the paper which is determined by the interfiber bond strength of the composite paper matrix. For machine-made papers, the latter is often sufficiently well oriented in the sheet plane to provide splitting in that plane ('2-d' sheet formation).

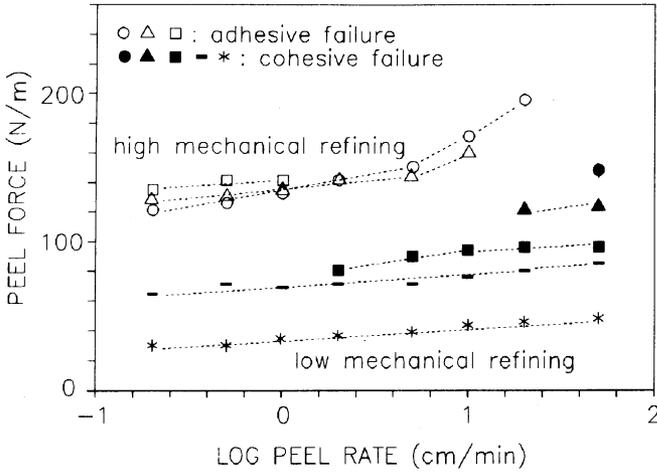


Fig 8-Peel force required to separate tape from sheets of fibers of different refining (from ref. 19).

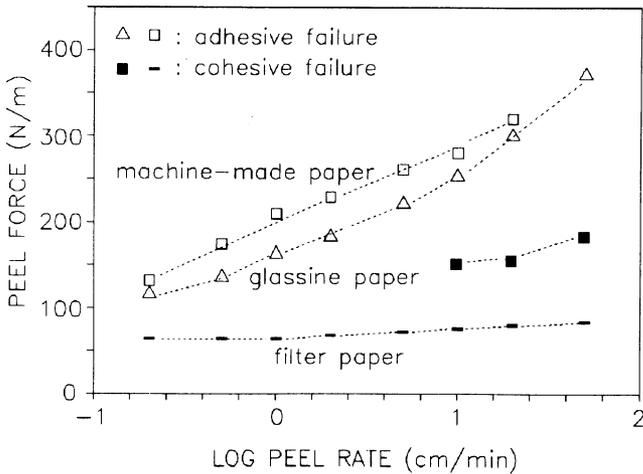


Fig 9-Peel force required to separate tape from different paper types (from ref. 19).

LIQUID WETTING AND PENETRATION

Many paper wetting and penetration studies have previously been presented at this conference series. A detailed review of these will not be given in this paper. Rather the application of wetting and penetration testing to the characterization of communication papers will be considered.

Commercially made communication paper provides an excellent substrate for dynamic sheet penetration testing using a Bristow testing device (20-22) or a similar design. The main draw-back is the time it takes to obtain a complete description of liquid uptake for each paper when several liquids are involved (23) (Fig. 10).

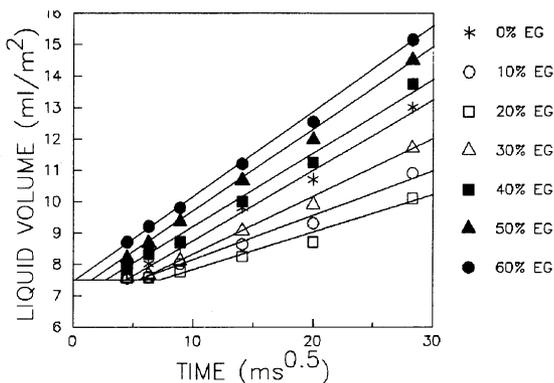


Fig 10-Penetration mode for an acid made, rosin sized paper. After a wetting delay, the liquid volume uptake varies linearly proportional to the square root of time (from ref. 23).

For sized communication papers, the liquid uptake V may follow the square-root relationship with time t shown in Fig. 10, that is:

$$V = K_r \quad \text{for } t < t_w \quad (3)$$

$$V = K_r + K_a (t^{0.5} - t_w^{0.5}) \quad \text{for } t > t_w \quad (4)$$

where t_w is the wetting time, K_r may be interpreted as \bar{a} roughness index, and K_a varies according to the following:

$$K_a \propto (\gamma/\eta r \cos\theta) \quad (5)$$

assuming that the fast-time sorption process is of mainly capillary nature (24).

That is, after initial wetting delay, the liquid uptake varies proportional to the ratio of liquid surface tension to viscosity γ/η , a mean effective pore radius r as a sheet structure term, and a $\cos\theta$ term that for analytical purposes may be correlated with the sizing treatment of the sheet (24). For the paper shown in Fig. 10, the effect of γ/η dominates over the effect of $\cos\theta$ causing K_a to decrease with the glycol content concentration up to 20%. Beyond this value, the effect of $\cos\theta$ becomes more dominant and the absorption rate increases with concentration (23) (Fig. 11).

However, many newer types of communication papers provide derivations from the variation shown in Fig. 10. This is particularly so for the alkaline made, synthetic sized copy and printing paper grades where only limited amounts of sizing agents have been added. Here, the short-time absorption rate can be shown to increase faster with time, and at a higher time exponent relationship if expressed similar to the previous variation (23) (Fig. 12 compared to Fig. 10). Fig. 12 shows much faster liquid transport away from the paper surface - a sheet functionality that affects both drying time and print quality in water-based ink jet printing (24).

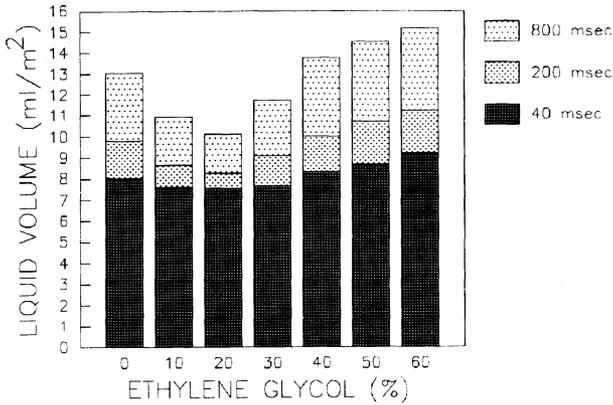


Fig 11-Cumulative liquid volume uptake at 40 msec, 200 msec and 800 msec. The liquid volume decreases with the glycol content up to 20%, whereafter it increases (from ref. 23).

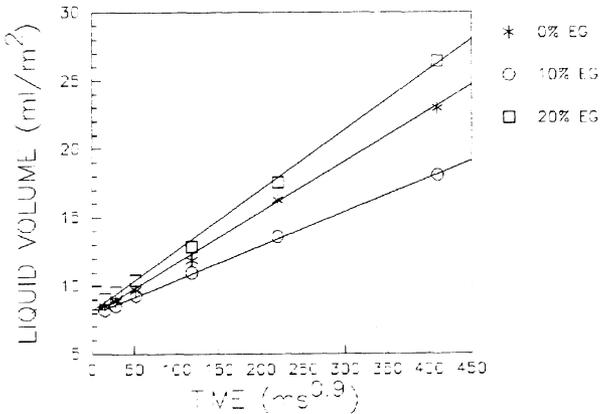


Fig 12-Fast penetration mode for an alkaline made, synthetic sized paper type (from ref. 23).

Drop spreading in ink jet printing is only simulated by high-speed dynamic liquid penetration testing even using identical inks and papers. At present, a theoretical treatment is lacking. Profile measurements for capillary spreading of organic liquids on paper suggest a penetration mechanism that is controlled by a time dependent redistribution of liquid from larger to smaller capillaries (25). Fast-time contact angle measurements of water droplets impinging on bond type papers show an oscillating drop variation at time of impact (26).

The water-based inks, that are of most interest to present ink jet technology development, are likely to penetrate by several mechanisms of which capillary sorption is only one (27). This makes dynamic wetting and penetration testing via the Bristow type instrument a correlation tool as many of the other characterization methods described in this review.

Other much simpler procedures are those that are static or long time dynamic. Liquid uptake test procedures similar to that used in Cobb size testing have been reported (28) to provide a variation in penetration uptake according to the penetration rate variation with liquid characteristics and sizing degree shown above, that is, a variation with surface tension to viscosity ratio and sizing degree to be considered in systems designs for ink jet printing. The variability, that sizing of copying and printing papers creates on fuse quality in the electrophotographic process, can be characterized using in-plane penetration testing as previously discussed at this Symposium Series (29).

Paper penetration testing using droplets of different viscosity and surface tension characteristics provides a fast method for comparing penetration behavior without carrying out quantitative dynamic penetration testing. Like for drop spreading on a solid surface (critical spreading concentration technique (30)), it is desired to define the liquid for which the transition from non-spreading

occurs. However, due to porosity, the liquid interaction with the paper is a three-stage process where initial wetting (no penetration) may be followed by basal and complete penetration pending on the liquid nature as shown in Fig. 13 (25).

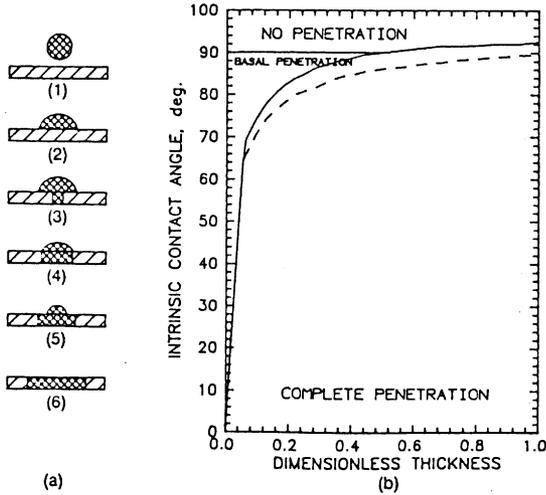


Fig 13-(a) Stages of drop penetration into a thin porous medium. (b) "Phase diagram" for penetration of a drop into a thin porous medium calculated based on thermodynamic analysis (from ref. 25).

In practice, an additional penetration stage is seen for most sized paper grades. 'Patchy penetration', somewhat similar to paper fiber feathering is encountered for most of the tested papers before basal penetration commences (31) (Fig. 14). This is not predicted by the model. Nor does the model account for other than capillary penetration into a homogeneous porous structure.

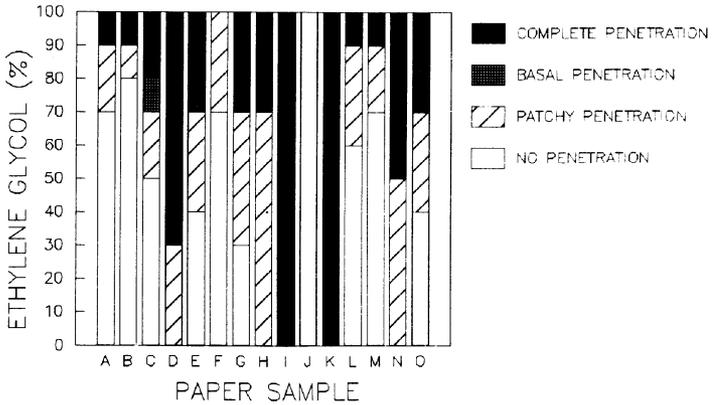


Fig 14-Critical penetration concentration map for a number of paper samples. The figure shows the ethylene glycol concentrations that provide the penetration states shown in Figure 13 (from ref. 25).

Ideally, contact angle analysis of commercially-made paper would require conditions of no penetration in Fig. 13. This is difficult to achieve since paper porosity causes penetration of many of the liquids traditionally used for, for example, Zisman critical surface tension analysis or other contact angle techniques (29). Using similar experimental conditions on different paper types, Zisman plots appear 's'-shaped (16) (Fig. 15). Simulating the sizing characteristics of alkyl ketene dimer (AKD) sized paper on cellulose films (32) generates relatively low critical surface tension values (Fig. 16). A summary of measurements on other cellulosic materials is shown in Table 2 (16).

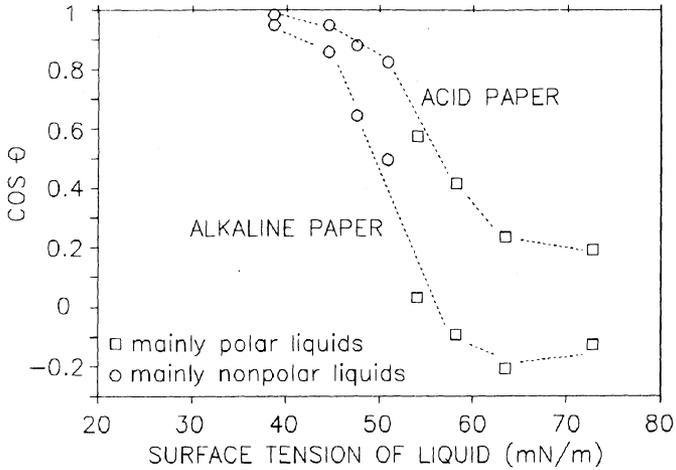


Fig 15-Zisman plot for acid and alkaline made papers (from ref. 16).

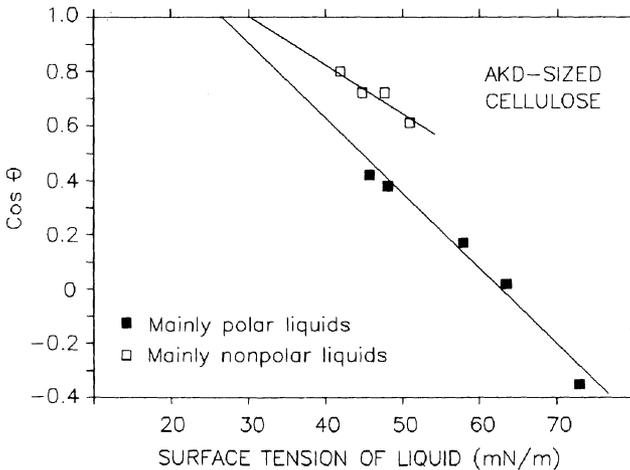


Fig 16-Zisman plot for alkyl ketene dimer sized cellulose simulating sized paper (from ref. 32).

Sample	γ_c (mN/m)	Ref.
Regenerated cellulose film	44	33
Unsanded wood	14.8-62.7	34
Sanded wood	52.0-83.2	34
Regenerated cellulose	45.0	34
Wood	14-47	35
Wood	47	36
Handsheets and machine-made papers	25-]60	37
Paperboard	31-48	38
Glassine paper	35-36	38
Regenerated cellulose films	35.5-49.0	39
Hemicellulose films	33-36.5	39
Microcrystalline cellulose (Avicel)	36	40
Wood (Douglas Fir)	52.8	41
Acid-made paper	38.7	42
Alkaline-made paper	33.5	42
Acid- and alkaline-made papers	24-43	43
Unsize cellulose film	39-52	32
AKD-sized cellulose films	22-36	32

Table 2. Zisman critical surface tension for cellulose films, wood and paper (from ref. 16).

The use of contact angle technique for the quantitative description of paper surface energetics would be desirable since it is a fast method that in the non-penetrating mode is not affected by the internal sheet structure. Unfortunately, both the porous substrate and the nature of the wetting liquid severely restrict its applicability.

INVERSE GAS CHROMATOGRAPHY

Solid surface energy analysis via inverse gas chromatography (IGC) relies on the thermodynamics of the adsorption process when hydrocarbons adsorb on the paper fibers (44). In this case, the adsorbates are carried through a gas chromatography column packed with paper chads, fibers or filler particles by an inert carrier gas at high dilution. The surface energy is calculated from mea-

surements of peak retention times for consecutive $((\text{CH}_2)_n$ and $(\text{CH}_2)_{n+1}$) alkanes. Since the alkanes penetrate the porous solids, energy values for plain paper are averages for external and internal solid surface. The use of non-polar adsorbates allows the determination of the dispersion energy component only.

IGC may be applied to the analysis of bond-type papers including those used as communication papers (5,29). When compared with other cellulosic solids, the variation in dispersion energy values is relatively large (Table 3). This may be due to both structural and chemical factors. For example, for solvent-extracted filter paper, molecular entrapment has been proposed to create increased interaction between the substrate and the gas molecules (48). The content of filler particles, such as calcium carbonate, may also tend to raise the paper energy (49).

Sample	γ_s^d (MJ/m ²)	Ref.
Cotton cellulose	48	44
Lignified wood fiber	37	44
Cotton cellulose	49.9	45
Cellophane	39-42	46
Bleached kraft paper	47.9	47
Bond-type papers	35.8-61.8	5
Unsize filter paper	45.7-48.4	48
Sized filter paper, unextracted	37.5-40.7	48
Sized filter paper, extracted	49.4-67.2	48

Table 3. Dispersion energy for cellulose, wood fibers, and paper samples determined by inverse gas chromatography analysis (from ref. 16).

Using polar probes, the IGC method can be extended to measure polar solid-gas interactions, also (48). While neither the analysis method nor the interpretation is as simple as when using non-polar alkanes, the method could be promising as a means of characterizing acid-base properties of

cellulosic solids including bond-type papers. As found for other materials (50,51) using the acid-base concept for cellulosic substrates may provide more insight into the thermodynamic characteristics of paper surfaces.

SPECTROSCOPIC ANALYSIS

A number of spectrometric analysis methods are being used routinely for paper analysis (52). This is particularly so when paper testing is supported by a broader materials analytical testing laboratory.

In addition to elemental analysis of surface constituents (53,54), ESCA (electron spectroscopy for chemical analysis) may be used for the quantitative description of the sizing level of communication papers (55-57). An increase in hydrophobicity as measured by the degree of C-H surface bonding would simulate the sizing uptake described by the stoichiometric oxygen-to-carbon ratio for most of the analyzed papers (57) (Fig. 17). This method is useful for characterizing the hydrophobicity of the surface structure in contrast to that of the complete sheet structure. Again, sizing degree would correlate with its functionality in paper adhesion as measured for toner images in electrophotographic copying (56) (Table 4).

Sample	Hydrophobicity (C1-%)	Relative fuse grade (%)
No sizing	18.5	100
Internal sizing	54.2	57
Internal/surface sizing	45.0	77
Light refining	19.2	76
Hard refining	13.7	96
No filler	14.0	94
Commercial #4 bond	32.8	76

Table 4. Hydrophobicity and relative fuse grade for bond-type papers (from ref. 56).

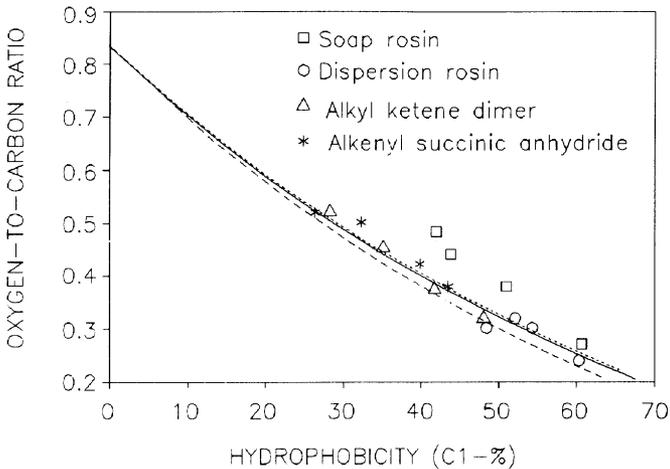


Fig 17-Decrease in oxygen-to-carbon ratio with increased hydrophobicity for different sizing types as measured by ESCA (from ref. 57).

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Transcription of Discussion

SURFACE CHARACTERISATION OF COMMUNICATION PAPERS

J Borch (Review Paper)

Dr S Loewen, Abitibi-Price Inc, Canada

Are Machine Direction vs. Cross Direction differences in surface characteristics important compared to manufacturing differences of bulk properties?

J Borch

No, it is generally less significant. Generally we do averages and there is not that much of a difference for the testing carried out.

Prof B Lyne, Royal Institute of Technology, Sweden

I was rather surprised to find that you were measuring the dispersive character of the paper surface when trying to predict the adhesion of a polymer or toner. The dispersive forces are a weak component of adhesion. Wouldn't it make more sense to measure the acid-base character of the surface which is the strong component of adhesion?

J Borch

It depends upon the polymer that you are using adhering to the paper surface. If you are looking at **(R2 D2)** the one example I showed, the ribbon is quite non polar, as a matter of fact. You are absolutely right if you are going to electrophotographic toners and these start getting polar, you are not seeing the complete picture. So again you have to consider the toner formulation, various

manufacturers have been using various kinds of polarity. In general we have been fortunate enough to just use the dispersive components.

Prof N Wiseman, UMIST, UK

You mentioned the importance of smoothness and commented that air leak methods seem to be the best means of measuring smoothness. However, there are several different air leak measurement techniques - Bekk, Sheffield, Bendtsen, Parker and possibly others as well. In the publication papers area it has been found that Parker is the most appropriate because of the relation between the land of the air leak barrier and the half tone dot. Can you comment upon any investigations, or what are your opinions, about the preferred method of air leak measurement for the sort of papers you have covered for this review?

J Borch

Yes I can easily comment on that. That is the Sheffield but the question you are raising is quite valid. The Sheffield has been used because it is traditionally used for bond papers. It is not because of any kind of technical question whether it is more appropriate or not. We have been doing Parker Printsurf measurements too and I think you would find, based on the data I have seen, that this would not create a large difference from the Sheffield variation in the kind of properties we have been measuring. There is generally a correlation between Parker and Sheffield but whether Sheffield is more appropriate or less appropriate – our data basically dictated what we can get from the industry and that is generally Sheffield.

Prof P Stenius, Helsinki University of Technology, Finland

You were commenting on the effect of making paper hydrophobic on friction. You were showing that friction was going down as you increased sizing which is very sensible. On the other hand you also commented on the influence of the chemical composition on friction of coated papers. Figure 7 in your paper shows that the kinetic friction goes up as oil absorption increases. This indicates, as I see it, that as the paper becomes more hydrophobic, friction goes up. Doesn't that indicate that in the case of this coated paper, at least, the mechanical factors must have a dominant influence on friction?

J Borch

The data shown were from plain papers and I think what Dr. Withiam suggests in the paper which was published one or two years ago, the added silicate is microporous and that would tend to take up the friction decreasing organic substances. So that is why the friction increases.

P de Clerck, Avebe (Far East) Pte Ltd, Singapore

Most of your work here has been related to papers that appear to be non-surfaced sized. In the Far East a very significant proportion of communication papers are surfaced sized mainly with starch based materials. Applying starches to the surface of the sheet affects greatly the surface characteristics in terms of the porosity, permeability, film thickness of the starch and the chemistry of the surface, depending on the type of starch that is used - cereal starches with a lot of fat and protein - potato and tapioca starches which are very pure and clean starches. The difference in surface characteristics that are produced by these starches - have you had

a look at the effect these have on the print quality?

J Borch

No, we have not but I would just like to correct you regarding surface size. Most of the papers we were using were surface sized in the sense that they were commercially available papers and the practice, as I understand it, is also to use starches for that. It is probably mainly the degree of surface sizing: we are really not adding that much surface size. We can see the effect on certain kinds of measurements using spectroscopic means but it seems to be mainly a level adjustment . The main variation is due to internal sizing. It is like adding a low level of oxidated or otherwise modified starch for that purpose. And, you are absolutely right, I would expect if you deliberately modify the surface with something that is very effective, a lot of these techniques would not be applicable in the sense that, for example, using IGC, you will be looking at both external and internal surface and you would not be able to measure external surface separately.

G Turner, Inveresk plc, UK

We have an interest in this concept of having high absorbency with a very smooth surface as in ink jet printing. You are referring to size press applications then, I just wondered if you could add any more advice with this because obviously we find in size press applications we tend to hold out rather than allow inks to penetrate and it is a combination of getting a good image but permitting the ink to penetrate on ink jet, which is the problem we have got. Any comment please?

J Borch

We have been looking at that aspect too mainly on commercially made papers that are desired to be used for ink jet printing in the States that lately have been marketed. Some of the paper manufacturers now put ink jet on the label and you may or may not find out that it works with your ink jet printer. In many cases it does not. Some of those that do not create the colour bleeding I demonstrated with the three roses, tend to be synthetic sized with relatively little amount of internal and surface sizing.