

# **Impact of Ink Paper Interactions on Printability of Aqueous Publication Gravure Inks. Part III: Acid/Base Interactions at the Paper/Ink Interface**

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**Keywords:** Acid/Base Interactions, Gravure Ink, Contact Angle, Stability, Paper, Surface.

## **ABSTRACT**

Changes in pH of water based inks and varnishes upon their contact with paper were investigated. Very thin films of the inks and varnishes were applied on the paper surface and their pH was followed within the first second of the contact. A mechanism responsible for acid-base reactions at the ink/paper interface and slightly beyond thereof was proposed. The impact of acid-base interactions on ink spreading on the paper surface was investigated using dynamic contact angle measurements. Properties of surface carboxylic groups of water based polymers were studied using a contact angle titration method and polymer solution/dispersion pH stability profiles. The acid-based reactions appeared to be very fast processes controlled by the rate of water penetration into the bulk of the paper and acidic ion diffusion from the paper into the ink/varnish film. However, the impact of these interactions on ink spreading on the paper surface was found to be secondary to the dynamic surface tension role. It was proposed that pH stability profiles of inks and varnishes could be useful in formulating ink for a given paper.

## **INTRODUCTION**

As with any printing process, quality of print obtained by the publication gravure process is in essence controlled by the physicochemical interactions between paper and printing ink. Spreading of the wet ink, as well as ink setting and drying are most directly impacted by these interactions. In the case of toluene based inks, the interactions are purely physical in nature, which greatly simplifies their analysis. With water based inks, however, the situation is much more complex. Water itself strongly interacts with all the components of paper including cellulose fibers, binders ( SBR latices of different carboxylation or PVA) and

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fillers (clay, calcium carbonate). The most obvious effect of these interactions is paper sheet distortion (surface and bulk), but there are also chemical effects resulting, most notably, in pH changes within the aqueous phase. As water based inks contain polymers which are usually pH sensitive, any change in the aqueous phase pH will result in profound changes within the ink film, leading to polymer/pigment precipitation, water release, viscosity increase, etc. The larger the pH differences between an ink and the aqueous phase in contact with paper, the more dramatic are these changes within the ink film. It is also important to relate all these phenomena to the time scale of the printing process. On a high speed gravure press, it takes anywhere from 100 to 300 milliseconds for the web to travel from the printing nip to the dryers. Any processes within the ink film which take longer than that are basically irrelevant to the print quality because any ink flow on the paper surface stops at the moment when the web is hit with the hot air. Moreover, none of the phenomena occurring within the ink film are independent of all the others, e.g., the rheology of the ink is determined by both pH changes and water release.

The literature on acid - base interactions between an aqueous phase and paper is rather scant and offers ambiguous conclusions (Triantafillopoulos et.al., 1992; Aspler et.al., 1992). The majority of the papers deal with ink transfer and resultant optical print density (Pshenichnikov et.al., 1980; Pauler, 1987) and none attempts to discuss the mechanism of the chemical phenomena taking place at the ink/paper interface shortly after it has been formed.

The purpose of this study was to investigate the acid - base interactions between water based publication gravure printing ink and paper and the impact of these interactions on the ink spreading and its stability. The experiments were performed using real printing inks and their individual components. Three different paper substrates (35lb SCA, 40 lb LWC and 60 lb heavy weight coated) were used. Measurements of pH within the ink film in contact with paper were done using pH color indicators. The impact of acid - base interactions on ink spreading was followed via contact angle measurements using a Fibro 1100 DAT Dynamic Absorption Tester. Stability of the inks and varnishes at various pH levels was determined by turbidity measurements. Properties of surface carboxylic groups were determined using a contact angle titration method.

## **EXPERIMENTAL**

### Determination of pH of Paper

The literature describes four methods of determination of paper pH. All were evaluated in the course of this study: (i) cold extraction, (ii) hot extraction, (iii) surface pH electrode and (iv) pH indicators method. None of these methods were suitable for determining "surface pH" of paper substrate relevant to the speed of

printing press. Therefore, a special method was developed based on premises similar to those of TAPPI Method UM 471. First, a rough estimation of paper surface pH was performed by preparing a series of pH indicator solutions covering a wide pH range, say from pH 3 to pH 8. The indicator solutions were drawn down with a #3 Mayer bar on the paper surface. The indicator color change was registered on video tape and then the pH was determined based on the video frame analysis. After that, an indicator pertinent to the pH of the given paper was selected and a series of reference buffered solutions of this particular indicator was prepared at pH intervals of 0.3. The reference solutions and the test indicator solution were then applied on the paper with a #3 Mayer bar and the pH of the paper surface was determined to an accuracy of 0.3 pH unit by comparing the color of the test solution to the those of the reference indicator solutions. The following pH indicators were used in this study: bromocresol green, chlorophenol red, bromothymol blue, phenol red, cresol red and bromocresol purple.

#### Determination of pH of Wet Ink Film

The pH changes within an ink film upon its contact with the paper surface were followed using a pH indicator method developed specifically for this purpose. Basically, a "pigmentless ink" was formulated with the addition of a proper pH indicator. Similarly, an indicator was added to a polymer solution or dispersion. Then a series of buffer solutions of the same indicator covering the pertinent pH range was prepared. Care was taken to assure that the concentration of the indicator in the buffer solutions and in the "ink" or varnish were the same. The buffer solutions and the "pigmentless ink" or the varnish were then applied on the paper surface with the #3 Mayer bar and the whole experiment was recorded with a video camera. This permitted evaluation of the color changes of the "ink", varnish or buffer solutions while in contact with paper as a function of time.

#### Determination of Contact Angles

To characterize spreading of inks and varnishes on a paper surface, contact angles of the ink, polymer solutions and polymer dispersions were measured using a high precision Fibro 1100 Dynamic Absorption Tester instrument. A water based acrylic ink, two different polymer solutions (a pH sensitive modified polyester and a pH-insensitive sulfonated polystyrene), and two polymer dispersions (a pH-sensitive acrylic and pH-insensitive polyester) were selected for the measurements. All these fluids contained 3% acetylenic diol surfactant to eliminate any impact of their inherently different surface tensions. In the contact angle titration measurements, thick films of respective varnishes were deposited on the Form 2A - opacity Leneta Board with a #13 Mayer bar. Contact angles of buffer solution droplets deposited on the dry varnish film surface were then measured using the Fibro 1100 DAT. The buffer solutions were prepared with surfactant free water and covered pH range from 1 to 14.

## Dynamic Surface Tension

Dynamic surface tension of the liquids studied was measured using a Sensadyne 6000 instrument by Chem-Dyne Research Corporation. Bubble rates from 4 to 7 bubbles per second were applied and results obtained for different systems were compared at the 5 bubbles per second rate.

## Stability of Varnishes vs. pH

The stability of polymer varnishes at different pH was determined by adding 0.1 ml of the varnish to 10 ml of a buffer solution in a test tube. In the case of polymer solutions, any instability was manifested by precipitation or coiling of the polymer and thus increased turbidity. When a polymer dispersion was added to the buffer solution of pH within its stability range, a simple dilution occurred and the liquid in the test tube became only somewhat more translucent. If the dispersion was unstable, coagulation of the polymer occurred and polymer aggregates settled to the bottom leaving a clear supernatant.

## RESULTS and DISCUSSION

Each of the four conventional methods for determining the pH of paper affords different information and is pertinent only to a specific application. Unfortunately, none of them provides information needed to analyze the quality of water based print produced on a high speed publication gravure press. Even TAPPI Method T 529, which does measure pH in a water droplet in contact with paper surface requires an equilibration time of about 2 minutes whereas the time allowed for publication gravure ink to spread and level at the paper surface is usually much less than 300 milliseconds. Moreover, the water droplet size used in Method T 529 is huge compared to the typical film thickness. Substantial differences between values of surface pH of the same paper obtained with these methods (including the one developed by us) illustrate our point (Table I).

The pH indicator methods are described in the literature as being successfully used for determining acidity of catalyst surfaces (Benesi, 1956), acid strength of surfaces (Walling, 1950) and in studies of acid/base properties of oxides (Carre et.al., 1992). The method of determining paper surface pH developed for this study allows for following pH changes within very short times. Even though this method is rather time and labor consuming and cannot be recommended for any routine paper testing, it has served our purposes very well.

<b>Table I</b>			
<b>pH of Papers Determined by Different Methods</b>			
<b>Paper</b>	<b>Method</b>		
	<b>Surface Electrode (1)</b>	<b>Cold Extraction (2)</b>	<b>pH Indicators (3)</b>
35 lb SCA	4.6	5.1	4.3
40 lb LWC	5.4	6.3	5.1
60 lb HWC	5.4	6.3	5.4
1) TAPPI Method T523 om - 82 2) TAPPI Method T509 om - 83 3) pH indicator method - as described in this paper			

Typical examples of equilibration of pH within varnish films upon their application on paper are presented in Fig.1. Two varnishes, one of very high and the other of very low acid number, and three papers (supercalandered A, 40 lb light weight coated and 60 lb heavy weight coated) were used. It is apparent that the pH within a varnish film changes very rapidly upon contact with a paper surface. After about 100 milliseconds, the rate of pH change slowed down substantially. We theorize that at the first moment of varnish contact with the paper surface, the liquid part of the varnish starts penetrating into the paper sheet. Interactions of the water phase with the components of the paper results in a pH change, usually a pH drop. The hydrogen ions released in the process diffuse into the varnish film, lowering its pH. Of the two processes, penetration is slower and thus determines the kinetics of pH changes. Knowing diffusion coefficient of the inorganic "acid" present in the system allows one to estimate the time needed for ions to penetrate across a varnish film of known thickness which is determined by the Mayer bar used. A precise determination of the diffusion coefficients is very difficult due to the complexity of the system. For a rough estimate, numbers of the order  $10^{-5}$  cm<sup>2</sup>/sec, quoted in the literature (Harned and Owen, 1958), can be employed. Based on these numbers, it can be calculated that the "acid" will penetrate a distance of the order of 1 micrometer into the ink film during one millisecond. Additional time of approximately a few milliseconds is needed for diffusion of the "hydrogen ions" across the ink film which is a few

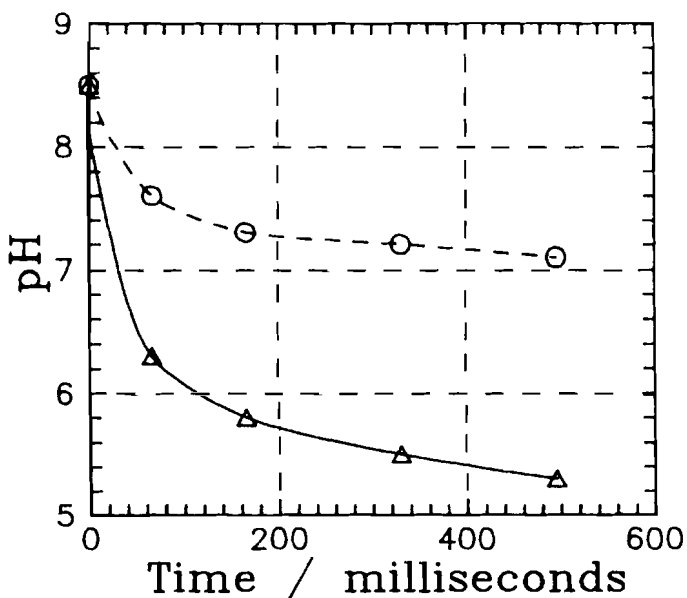


Fig. 1. pH of polymer solution film in contact with SCA paper vs. time; (O) high acid number, (Δ) low acid number.

micrometers thick. An exact determination of this time is very difficult because at least several “acids” of different diffusion coefficients are involved and the viscosity of the environment also changes simultaneously. The estimated diffusion time, however, agrees roughly with the rate of pH changes within the varnish films. There are also significant differences between the pH curves obtained for varnishes of low and high acid numbers, which result from different amounts of acid needed to precipitate a given polymer. The curves in Fig.1 suggest that more acid is needed to precipitate a varnish of higher acid number, as the final pH of this varnish film was higher.

Kinetics of pH changes within a “pigmentless ink” drawn down on different papers is presented in Fig.2. The general run of the curves is very similar to those in Fig. 1, and the shift of the curves is related to the different amounts of the total “acid” extracted from the different papers.. Again, diffusion of the acids to the ink film seems to control the rate of the total process. Uptake of “acids” released from the paper will take place at first in the layer of ink film which is in direct contact with paper. Therefore the properties of this layer can be different from those of the remainder of the film.

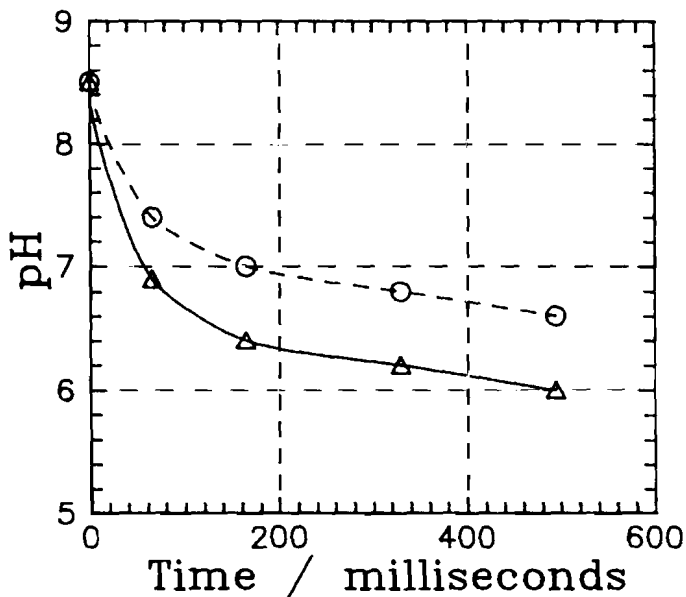


Fig. 2. pH of WB acrylic ink film in contact with paper vs. time; (O) less acidic paper, (Δ) more acidic paper.

Obviously, a drop in pH below the polymer stability range should have an impact on the ink spreading on the paper. To observe the impact of pH on ink spreading, two polymers were selected: one sensitive to pH changes within a range of pH 5 to pH 7 (modified polyester) and another which was water soluble within the whole pH range. Two dispersion polymers were selected the same way, i.e. an acrylic sensitive to pH changes within the range of 6 to 8, and polyester not sensitive to pH changes over a wide pH range. Our earlier work indicated that these polymers exhibited very different behaviors with respect to absorption by paper substrates. The polymer sensitive to pH penetrated into the paper much slower than that insensitive to pH (Sprycha and Hruzewicz, 1995). The contact angles of polymer solutions and dispersions on SCA paper vs. time are presented in Figs. 3 - 5. The description of varnishes is presented in Table II.

It is to be noted that physical properties of all the varnishes were very similar except for the modified polyester which had a higher dynamic surface tension (DST) value, despite all varnishes having the same (and very high) percentage of the surfactant. This very interesting phenomenon is a subject of separate studies in our laboratory.

The differences in contact angles between modified polyester and sulfonated polystyrene as shown in Fig.3 result from both acid-base interactions and

**Table II****Properties of the Liquids Used (3% surfactant level)**

Fluid	Type	Shell #2 Cup Viscosity (sec)	pH	Dynamic Surface Tension (dynes/cm)**
Modified Polyester	Polymer solution	20	7.5	40
Sulfonated Polystyrene	Polymer solution	20	7.5	30
Modified Polyester	Polymer solution	20	7.5	60*
Sulfonated Polystyrene	Polymer solution	20	7.5	60*
Acrylic	Polymer dispersion	20	8.3	30
Polyester	Polymer dispersion	20	8.3	30
*surfactant free samples				
** DST at 5 bubbles /sec.				

DST. The DST values of surfactant free modified polyester and sulfonated polystyrene were the same at about 60 dynes/cm. Their contact angles on SCA are presented in Fig.4. Now, the differences between these varnishes are smaller and can be ascribed to differences in acid - base interactions only. Contact angle vs. time relationships (for these two polymers on 40 lb LWC and 60 lb HWC substrates) are very similar to those presented in Figs 3 and 4. The differences between the two polymers became smaller on LWC and yet smaller on HWC papers. This can be easily explained by an increase in pH of the papers in the series SCA, LWC and HWC (Table. I).

The contact angle vs. time relationships for the polymer dispersions (Fig.5) are very similar to those obtained for polymer solutions. Kinetics of the two phenomena i.e. 1) the acid-base interactions between the ink film and the substrate and 2) the sorption of liquid by paper are of paramount importance



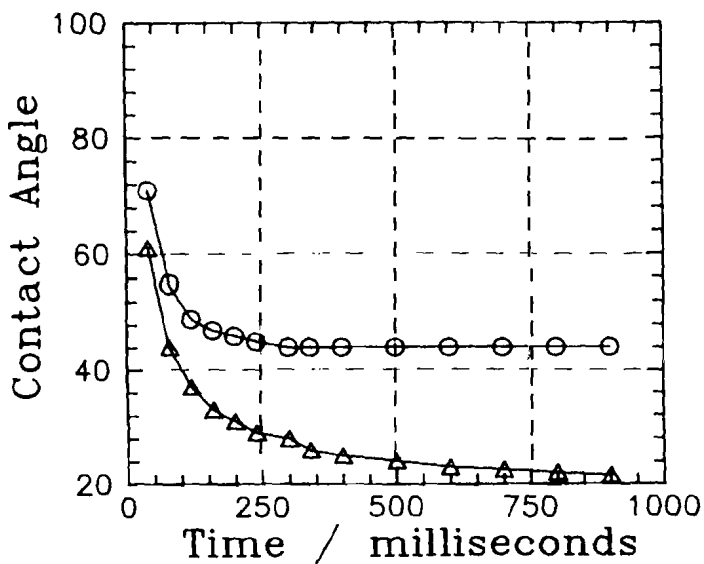


Fig. 3. Contact angle vs. time; (O) modified polyester DST= 40 dyne/cm, ( $\Delta$ ) sulfonated polystyrene DST=30 dyne/cm.

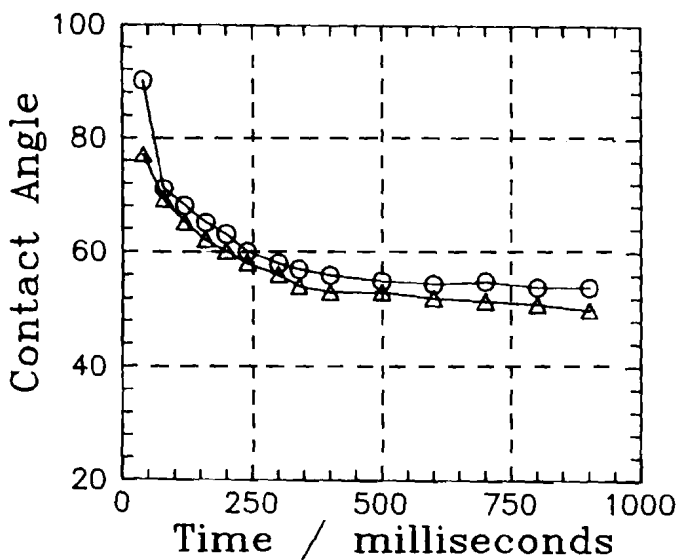


Fig. 4. Contact angle vs. time; (O) modified polyester DST=60 dyne/cm, ( $\Delta$ ) sulfonated polystyrene DST=60 dyne/cm.

to the ink spreading. At the first instant of contact between the ink and paper, only a limited amount of "acidity" from the very paper surface is available for reaction with the ink film. Further amounts of the acid become available as the aqueous phase penetrates into the bulk of the paper. It was reported by others that the penetration is initially slow and accelerates with time (Salminen, 1988; Lyne and Aspler, 1982) - a phenomenon referred to as a "wetting delay" by some (Lyne and Aspler, 1982) and as a "penetration delay" by others (Sprycha and Hruzewicz, 1995). This further slows down the acid-base interactions under consideration. The amount of acidity needed to completely neutralize the ink film depends on its thickness as well as on its buffering capacity. For instance, polymers of high acid number will consume more paper acidity. Furthermore, buffers can be added to the ink formulation to modify its spreading behavior.

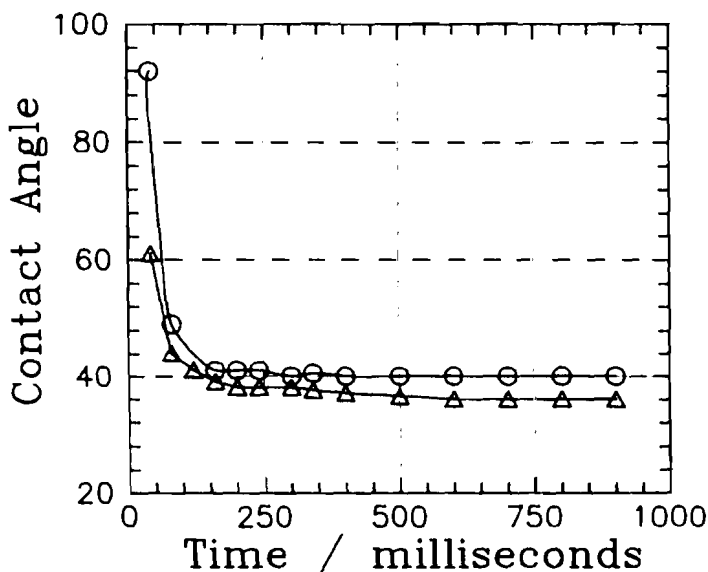


Fig. 5. Contact angle vs. time; (O) acrylic dispersion DST=30 dyne/cm, (Δ) polyester dispersion DST=30 dyne/cm.

Spreading time of a liquid, impact of the droplet size, dynamic surface tension and effect of viscosity of the liquid on ink spreading, can be determined with a high speed camera (preferably 1000 frames/second or faster) which allows for measuring the base of the droplet vs. time of contact. Unfortunately, the Fibro 1100 DAT was the fastest instrument we had at our disposal and was too slow for this application at 50 frames per second capability. Based on Fibro 1100 DAT data we evaluated the time of spreading of surfactant-free 8-9 microliters and 1.5 microliters water droplets on the Leneta board at about 30 and less than 10 milliseconds, respectively. Even very rough extrapolation indicates that the spreading time of the minute droplets of ink coming out of a gravure cell a few tens of picoliters in volume is 1 millisecond or less. Obviously, this estimation is

very rough and neglects factors such as ink viscosity changes at the ink/paper interface. Nevertheless, in the very first moments of ink - paper contact, DST plays a dominant role in the spreading phenomenon and acid-base interactions predominate later. Curves in Figs. 3 - 5 illustrate this discussion. It is important to remember that whatever happens within the ink film or at the ink /paper interface after the first 200 - 300 milliseconds has no impact on printability or spreading.

Acid-base interactions can cause destabilization of the polymer solutions or polymer dispersions. Precipitation of a given polymer occurs at a certain pH due to a specific property of its carboxylic groups which provide for its solubility or dispersibility in water. The dissociation constant (K) quantitatively characterizes the carboxylic groups:



$$K = \frac{[R - COO^{-}] [H^{+}]}{[R - COOH]} \quad (2)$$

The higher the value of the dissociation constant, the more dissociated is the acid. Determination of the dissociation constant of water soluble acids is relatively simple, as the concentration of  $H^{+}$  ions can be easily measured with great precision. In the case of surface carboxylic groups, however, concentration of  $H^{+}$  ions in the interfacial region can not be measured. Moreover, the environment of the carboxylic groups is very different from that in the bulk of aqueous solution. The dielectric constant of an organic polymer is much lower than that of water, so the dielectric constant within the interfacial region most probably falls somewhere between these two, even though it is difficult to estimate its actual value. In the opinion of many authors (Berg, 1993; Whitesides et.al.,1991), the surface -COOH groups are more difficult to ionize because of the dielectric constant of the interfacial region being lower than that of water.

Because of all the difficulties associated with determining the dissociation constants of surface -COOH groups, a  $pK_{1/2}$  value has been introduced which is defined as the pH of a bulk solution at which the dissociation degree ( $\alpha$ ) of surface -COOH groups is 0.5:

$$\alpha = \frac{[-COO^{-}]}{[-COO^{-}] + [-COOH]} \quad (3)$$

The value of  $pK_{1/2}$  can be estimated from the contact angle of water at different pH values on the surface of a given polymer. This technique is called the contact

angle titration. The relationship between contact angle and dissociation degree is given by the following equation ( Berg, 1993):

$$\alpha = \frac{\cos \theta - \cos \theta_{\max}}{\cos \theta_{\min} - \cos \theta_{\max}} \quad (4)$$

where:  $\theta$  - contact angle at a given pH

$\theta_{\max}$  - maximum value of contact angle (nonionized surface)

$\theta_{\min}$  - minimum value of contact angle (totally ionized surface).

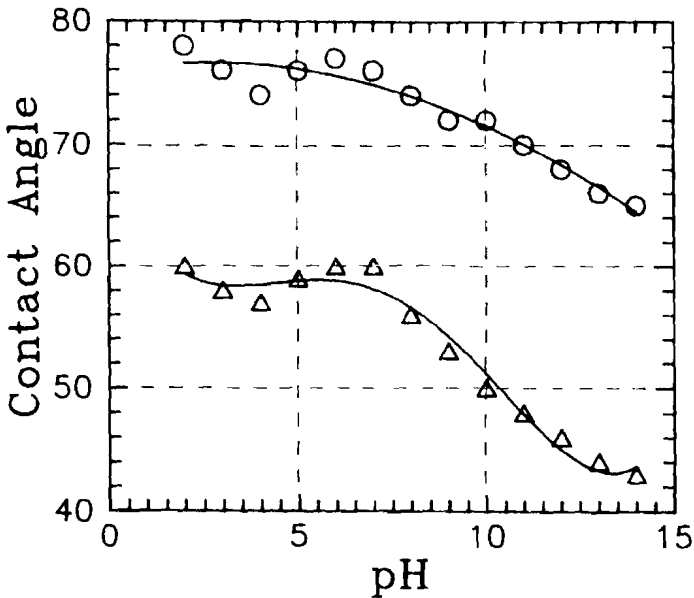


Fig. 6. Contact angle titration; (O) acrylic dispersion, ( Δ ) surfactant free acrylic dispersion.

The contact angle titration technique was originally developed to characterize the surface -COOH groups of plastic films, e.g. corona treated polyethylene films (Holmes-Farley et.al., 1988). We used this technique to characterize surface -COOH groups of film forming WB polymers. The results obtained with two commercial acrylic varnishes, one of which was surfactant free, are presented in Fig. 6. The contact angle for both materials decreased with increasing pH of water, the difference  $\theta_{\max} - \theta_{\min}$  being bigger for the surfactant free varnish. This probably was due to absence of a surfactant which masks the impact of an acid-base reaction on the contact angle value. In general, the run of these curves was very much similar to that characteristic of polyethylene films (Holmes-Farley

et.al.,1988). Based on these curves, values of  $pK_{1/2}$  for the varnishes can be calculated using Eq. (4).

Stability profiles of chosen polymer solutions and polymer dispersions are presented in Figs. 7 and 8 respectively. The information on polymer stability vs. pH is very important for an ink chemist.

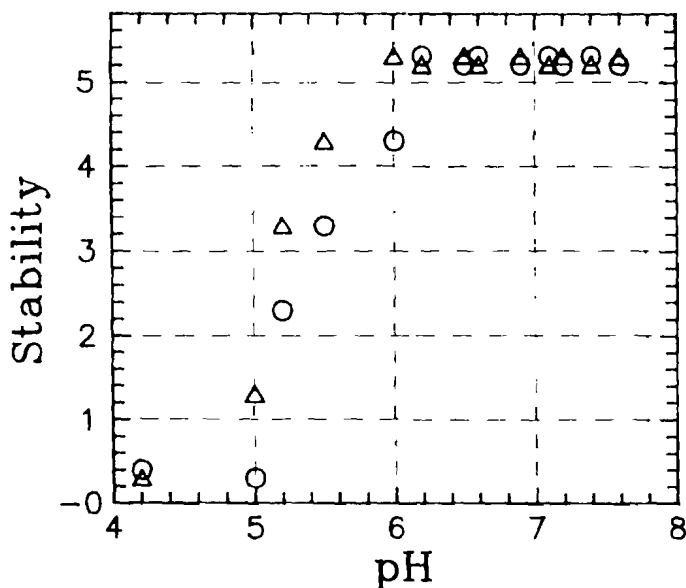


Fig. 7. Stability profiles of polymer solutions; (O) modified polyester, ( $\Delta$ ) acrylic. Arbitrary scale - 0=unstable; 5=very stable.

Obviously, during ink manufacture, storage and shipment, the pH of the ink should be well within the stable pH region. During the printing process, however, it may be very advantageous to incur some sort of instability at certain point, either to speed up the solvent (water) release, or to obtain a desired printability or a dry ink film property. There is an adage popular among ink formulators that the best inks are usually at a verge of stability disaster. Especially in the case of printing on acidic substrates such as most papers, the pH of ink film deposited on the paper may well drop below its lower stability limit, resulting in great impact on the ink spreading and water release. Moreover, some polymer precipitation at the ink/paper interface may result in blocking of water penetration into the substrate. This may advantageously reduce or eliminate paper distortion, but adversely slow down the ink drying.

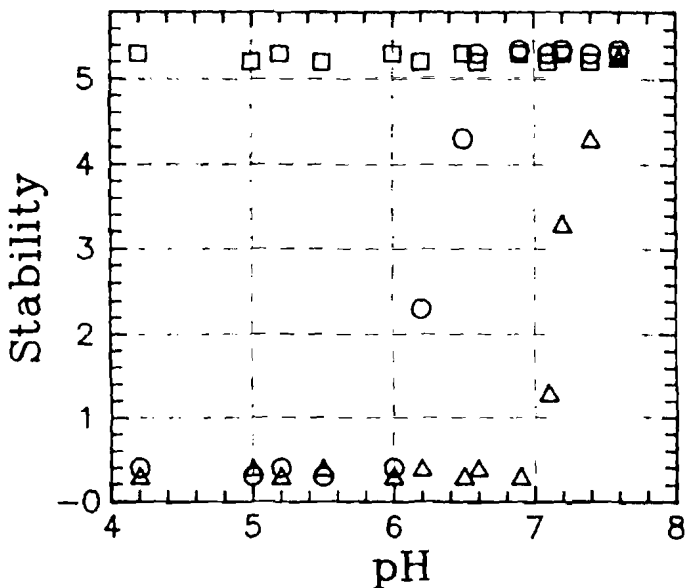


Fig. 8. Stability profiles of polymer dispersions; (O) surfactant free acrylic, ( $\Delta$ ) acrylic, ( $\square$ ) polyester. Arbitrary scale - 0 = unstable, 5 = very stable.

The data presented in Figs. 7 and 8, either obtained from the polymer supplier or from our own measurements, are helpful in predicting what may happen upon contact of ink with paper of known pH.

## CONCLUSIONS

Data presented in this paper are far from exhausting the issue of acid-base interactions at the ink/substrate interface. However, some understanding and clarification of their impact on print quality has been achieved. We think that importance of this issue and the necessity of further work has been demonstrated, and illustrates a way of improving the print quality of water based publication gravure printing. The following are the most important conclusions:

1. Drop in pH of water based ink upon contact with paper results from acid-base interactions of these two media. The pH drop occurs very rapidly and its rate is controlled by diffusion of acidic ions from the paper into the ink film.
2. The amount and rate of "acid" generation in the paper in contact with the ink film depends on the rate of water phase penetration into the paper and on its interaction with the paper components.
3. The higher the acid number of a polymer, the bigger its buffering capacity and its resistance to pH changes.

4. The impact of acid-base interactions on ink spreading seems to be secondary to that of surfactants present in the ink. The greater the pH difference between the ink and the paper, the more significant the acid-base interaction contribution to the ink spreading.

5. Acid-base interactions have a profound impact on water penetration from the ink film into the paper substrate.

6. Spreading of ink on a paper surface is faster with very small ink droplets. In case of droplet volumes on the order of that of a gravure cylinder cell, the spreading time seems to be shorter than 1 millisecond. Unfortunately, we did not have a fast enough camera available to record the spreading accurately.

7. "Stability profiles" of a water based ink vs. its pH are very helpful in formulating an ink for a given paper substrates.

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