Hot extended press nips as gas-phase reactors: hydrophobation with ASA

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ABSTRACT *Hot extended nips could be used as self-sealing reaction vessels for gas-phase modification of dry paper webs. This possibility is illustrated by the gas-phase redistribution of an ASA (alkenyl succinic anhydride) and an AKD (alkyl ketene dimer) sprayed onto one side of an unsized paper before the nip. This method can become an alternative to wet-end sizing for specialty papers. A simultaneous auto-crosslinking of paper polymers also occurs.*

On a 160-g/m² unsized web of 94% solids content, a nip of 100 ms and 0.4 MPa produced an excellent two-sided hydrophobation with 0.06% ASA sprayed onto one side, when both sides of the hot nip platens were at 240–260° C. With a nip of 200 ms and 5 kPa, a temperature of 350° C was required on both sides to achieve this redistribution. With the AKD used and a single-side hot nip of 100 ms and 0.4 MPa, a temperature of 300–350° C on the sprayed side was required for a full redistribution. Data are also given for webs of 74% ingoing solids content.

KEYWORDS
Extended nip pressing
Hot pressing
Moisture
Pressing
Sizing
Water resistance

Hot press nips such as roll nips, extended shoe nips, or band presses in paper machines or paper converting operations provide, for an extremely short period of time, a closed pressure chamber with a reasonable degree of sealing. If the temperature is high enough, chemical reactions can occur, including gas-phase reactions and redistribution. Such reactions are especially prone to take place with low-molecular-weight organic components (with resin and fatty acids, for example), which originate from the wood extractives or are added for sizing. The amorphous paper polymers are chemically activated or physically softened if the temperature rises above their respective glass transition temperatures.

A temperature gradient through the paper is developed in a hot nip. Depending on the conditions chosen, the chemical reactions can be concentrated on one or both sides of the paper web. The web can be dry, or it can be moist with water vapor acting as an important gas-phase component. In the initial part of the hot nip, this water vapor also facilitates heat transfer into the sheet.

Three main types of processes can take place either separately or together:

1. A redistribution and a chemical anchoring of low-molecular-weight oleophilic components on the fiber surface (*1, 2*)
2. Crosslinking of wood polymers, involving for example auto-crosslinking in the presence of oxygen or involving crosslinking chemicals such as aldehydes and promoted by catalysts (*3, 4*)
3. Changes in the web structure giving greater smoothness or a greater bonding area or causing a densification of the paper web, such as brought about in hot calendering (*5, 6*).

Chemicals can be applied to the web before the hot nip by different means—by offset print rolls, by an airless pressure spray, or with compressed air combined with an ultrasonic atomizing nozzle, for example.

Here, we discuss the potentials and restrictions of such extended hot nips. Data are presented from experiments conducted on the gas-phase hydrophobation of paper, using an alkenyl succinic anhydride (ASA) and an alkyl ketene dimer (AKD) sprayed onto one side of the paper before the hot nip.

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Known gas-phase reactions for modifying paper

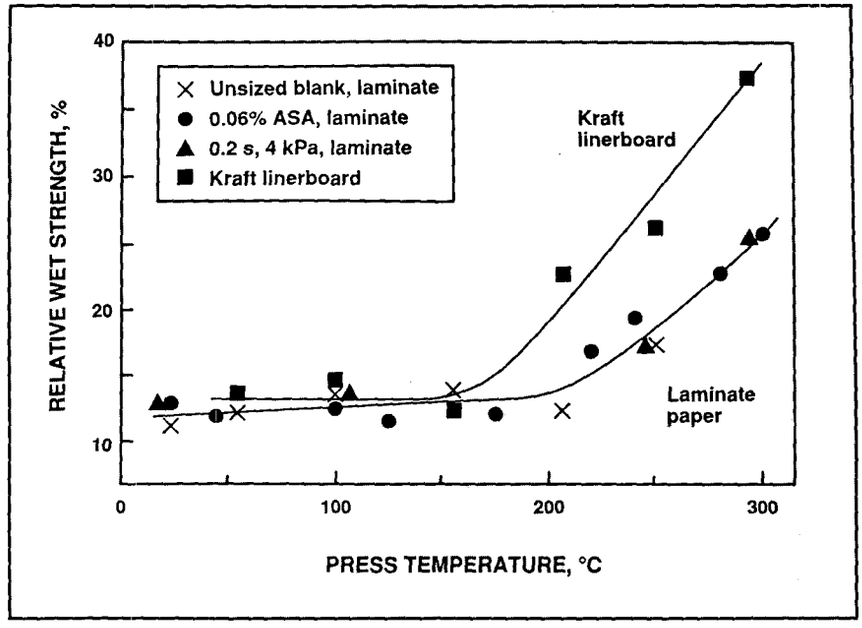
The spontaneous gas-phase hydrophobation of paper by the redistribution of low-molecular-weight oleophilic material during storage has been recognized for more than 40 years. The anchoring of redistributed fatty acids to aluminum, ionized or hydroxidized at the cellulose surface, considerably improves this hydrophobation rate (*1*). Such anchoring also prevents the overturning of these fatty acids on wetting (*2, 7*); consequently, the permanence of water repellency is increased.

Spontaneous redistribution of oleophilic components also takes place by diffusion to a hydrophilic polymer surface from its solid interior or by absorption from the surrounding air. Such a redistribution is shown on Corona-oxidized paper surfaces during subsequent storage at room temperature (*8*). If the oleophilic material within the paper is well anchored to the hydrophilic surfaces, less of it is available for redistribution (*8*).

Another spontaneous reaction is the auto-crosslinking of paper—that is, of wood polymers during storage in the dry state (*3*) and in the presence of moisture (*9*). As a result of auto-crosslinking, the press drying of paper at high temperatures leads to increased wet strength (*10*). Also, wet strength resins and phenolic resins crosslink fibers already in the moist state (*11*). Such crosslinking and auto-crosslinking has a complicated reaction mechanism (*12*), since chain cleavage occurs as well. The reaction rate of auto-crosslinking roughly doubles per 8°C temperature increase (*3*). Thus the outgoing web temperature from a nip with much hotter press surfaces is one indication of the degree of reaction (*4*).

Figure 1 depicts this spontaneous auto-crosslinking effect as it occurs in the 100-ms, 0.4-MPa hot nip we used. The effect is independent of any addition of ASA. These auto-crosslinking reactions occur between chains both in the hemicellulose and lignin polymers—such as in the fiber-fiber bonding area to produce wet-strength interfiber bonds. After activation by heat, causing partial oxidation and the formation of radicals, then interchain bonds, ether bonds, and hemiacetal bonds are formed. As a consequence, the Cobb values are slightly reduced, as we see for the blanks without ASA in most of the figures presented here.

1. The auto-crosslinking effect, evaluated against press platen temperature as the relative wet strength after 24 h of immersion. (All data points except triangles refer to 0.1-s, 0.4-MPa nips.)



Various gas-phase reactions to modify paper by adding chemicals have been studied over the last 30 years. Examples are crosslinking by formaldehyde (*13*) or by diisocyanates (*14*) such as hexamethylene diisocyanate and gas-phase hydrophobation of paper by added fatty acids (*15-17*), by alkoxysiloxanes (*18*), or by alkylsilicon halides (*19*). Gas-phase hydrophobation of the dried paper does not interfere with the interfiber hydrogen bonding during drying. Therefore it permits the papermaker to produce a strong paper together with a good hydrophobation of the reactive surface area. To our knowledge, none of these gas-phase hydrophobation processes have become commercial, partly because of the complexity of the process on a paper machine. Hot extended nips, as described here, are alternative reactors for these processes.

Redistribution over a paper or paperboard of volatile flame retardants such as boric acid (*20*) might also be possible in a hot extended nip.

A hot extended nip as a gas-phase reactor

At today's paper machine speeds, hot nips with pressures of a few MPa have a retention time of up to 10 ms for common press roll nips or up to 40 ms for shoe press nips of about 0.25 m. Longer, double-band press nips are not yet commercially available for paper machine speeds, but they are available for building board and paper converting at speeds up to a maximum of about 100 m/min. With steel or plastic belts around a gas-fired cylinder, pressures of a few hundred kPa [400 kPa in the Pira rig for example (*21*)] at higher speeds are available, extending the nip length to 2-3 times that in a shoe press. These presses could be developed to employ entrance temperatures for the roll or band nips of up to 400°C. Web exit temperatures and gradients depend on the heat consumption in the nip, the evaporation of water and oleophilic material, the heat content of the equipment, the web thickness and grammage, etc. At higher moisture contents, the nip temperature must be kept lower to avoid delamination of the paper web at the nip exit (*22, 23*).

All these nips can be considered to be self-sealing continuous gas-phase reactors, provided the mechanical pressure is sufficiently larger than

the vapor pressure of the chemicals and moisture present. Temperatures on each side of the paper, temperature gradients through the paper (affected by the applied mechanical pressure), and nip retention times are reaction variables. Not only is the nip pressure necessary for sealing, but it also affects the contact area and heat transfer coefficient, as well as heat conductance by virtue of compression of the web. As a consequence, the applied nip pressure had some effect on auto-crosslinking at 204°C (*9*). For many reactions, the nip pressure required is in the range of only 10–100 kPa.

The temperature within the nip is the simplest variable with which to adapt the reaction rate to the nip dwell time available. It determines the vapor pressure of the volatile reactants and thus their diffusion rates. The temperature also determines the rate of reaction or anchoring. Temperature gradients in the paper can be useful or obstructive. If no anchoring reactions occur, the temperature may determine the amount of absorbed oleophilic material, since the absorption isotherm varies with temperature. Several reactions can take place simultaneously, such as an auto-crosslinking reaction together with a gas-phase redistribution of low-molecular-weight material.

The reactions must have almost ceased within the available nip reaction time to avoid the loss of vaporized material. As in all vapor-phase reactors, factors such as safety conditions and ventilation have to be considered. The mechanical pressure applied, especially the maximum pressure of the press pulse, also has an effect on the development of paper densification and surface smoothness at a given temperature.

Here, we examine this use of extended hot nips, with nip platen temperature as the main variable for the gas-phase redistribution of ASA for the hydrophobation of paper.

Experimental methods and materials

Process conditions

Extended press nip conditions of 100 ms (± 10 ms) retention time and a pressure of 0.4 MPa were chosen for the main part of this work. For the most part, we used a flat platen press preheatable up to 450°C and having four pneumatic pistons and a maximum pressure of 6 MPa (*22*). With the shoe length of 0.25 m, this retention time would correspond to a web speed of 150 m/min, a common speed in some converting machinery.

The paper samples were inserted between two chromium-plated gloss plates, with both or only one preheated to the surface temperature, as measured with thin thermocouples. For some experiments, a press simulator of the hammer and anvil type (*24*) was employed. This simulator was modified with a preheated exchangeable hammer plate and the cold anvil (*5*) and was useful for nip retentions up to 20 ms. For one set of data, we used a semi-manual 200-ms nip of 5 kPa·s with two electrically preheated plates.

Paper material

As paper material, an unsized 162-g/m^2 unbleached kraft paper for press laminates was used for most of the experiments. Its density was 700 kg/m^3, and its Bendtsen air permeance was 370 mL/min. Its extractive contents was 0.30% as determined with chloroform and 0.16% as determined with acetone.

To the paper, 0.05% of urea resin had been added to increase wet strength. In a two-sided, 100-ms hot nip, this paper develops some additional wet strength, as indicated in Fig. 1, and a minor loss in the Cobb value, as seen for the blanks in subsequent figures. The water penetration rate (measured as the sorption height according to Klemm for 10 min) was not affected. However, the amount of water absorbed from the cut edge (during the 10 min interval) was reduced to 83% and to 66% of the value of untreated paper at 255°C and 295°C, respectively, as a result of swelling restrictions.

A 150-g/m^2, dispersion-sized kraft linerboard was used in a few experiments.

Chemicals

Chemicals added for gas-phase redistribution were an alkenyl succinic anhydride (ASA), sold in Scandinavia under the tradename "Accosize 18" by Berol (now Nobel Paper Chemicals). In some cases, this ASA was applied as water dispersion stabilized with cationic starch, but in most experiments it was applied as a mixture of 60–80% pure compound and 40–20% by weight of acetone. Acetone was added only to reduce the viscosity at 20°C from above 200 mPa·s to 50 mPa·s to permit laboratory spraying.

The melting point of this ASA product was given as -7°C to -4°C, and the boiling point was given as 396°C. Since this product has a viscosity of 100 mPa·s, at 40°C, it appears to be possible to spray it directly onto the web without solvent in commercial equipment. When the aqueous emulsion of the ASA, containing about 1% starch, 1.5% Accosize 18, and 97.5% water was applied, the paper solids content dropped to about 85% going into the hot nip.

A few experiments were carried out with an alkyl ketene dimer sold in Scandinavia by Hercules under the tradename "Aquapel 364." It had a melting point of 42°C and a boiling point exceeding 300°C, applied as a 9% solution in acetone.

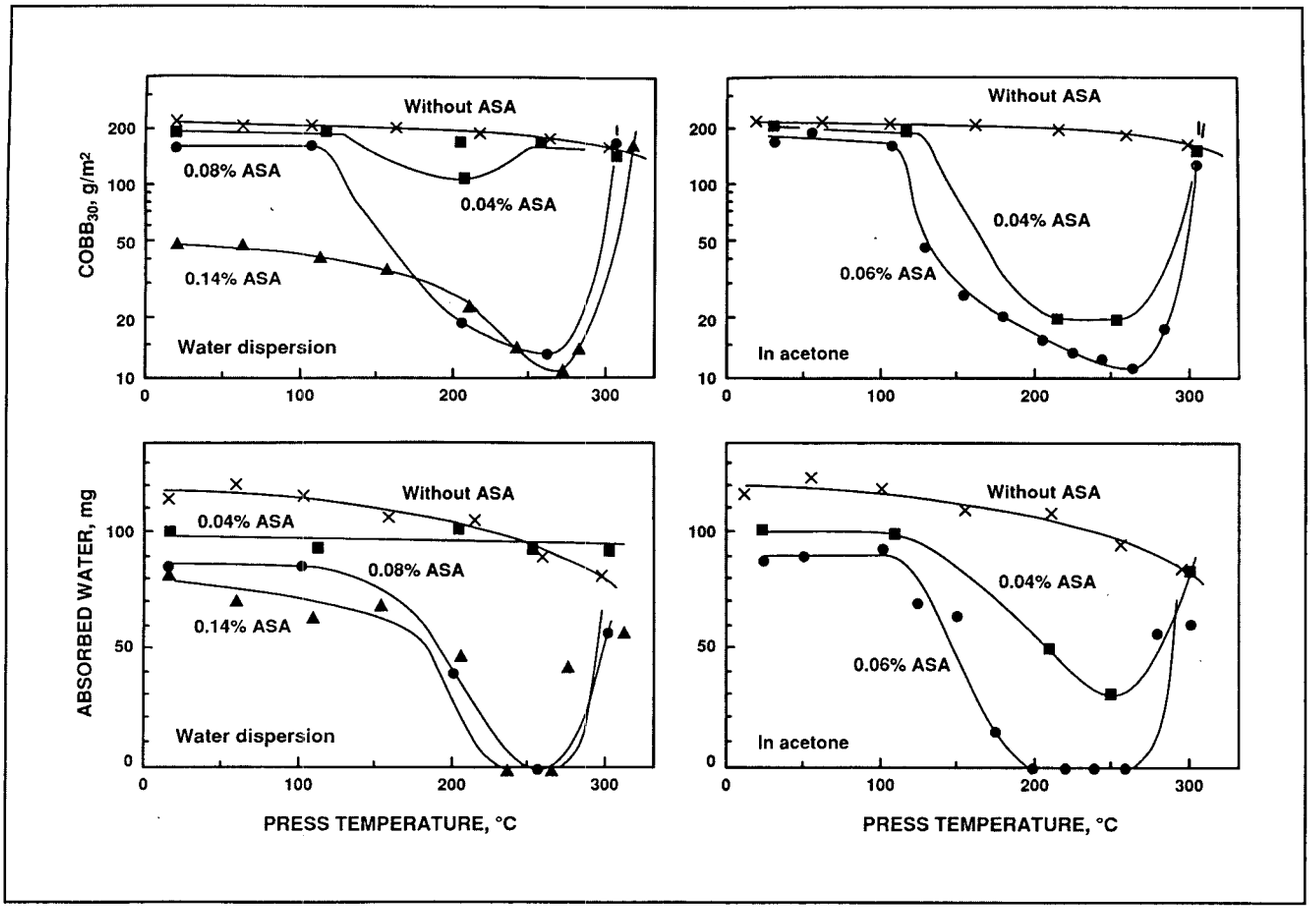
These chemicals were applied to the wire side of the laminate paper. Information concerning the vapor pressure of these compounds as a function of temperature was not available.

Spraying

To spray these chemicals, we used an electrically driven, high-pressure, airless, paint spray gun (Wagner W320) with a flat nozzle. The slit direction was perpendicular to the direction in which the paper web was moving, and the flow was approximately 30–70 mL/min. The spray gun was stationary, and the paper sample was drawn past, usually at 150 m/min.

On the sprayed paper samples were visible droplets of 1–2 mm in diameter. Their disappearance in the hot nip was a visible measure of redistribution. The amount of applied solution was determined by weighing the paper; in some cases, it was checked by spraying it on aluminum foil. Hot press nips were applied within a few seconds after spraying. In a few cases, for the sake of comparison, the sprayed samples were stored at room temperature for one week before the hot nip was applied.

2. The effect of a 0.1-s, 0.4-MPa, two-sided hot nip on the water repellency of an unsized laminate paper sprayed with a diluted starch-stabilized water dispersion of ASA (left) and with ASA diluted with 20–40% acetone (right). (Water repellency as Cobb 30 s as well as absorbed water from the cut edge in milligrams, by 15 mm wide, immersion time of 10 min.)



Test methods

In the test methods, SCAN standards were followed unless otherwise stated. Samples were conditioned overnight at 23°C and 50% RH before testing.

Static contact angles were measured according to SCAN-P 18:66. The Cobb values after 30 s and 60 s were measured according to SCAN-P 12:64. The Cobb values after a water contact time of 30 min with a blotter beneath the samples were measured according to a method by TNO Delft (*25*), in which the absorbed water is reported as that in paper plus that in the blotter. The edge suction height was measured according to SCAN-P 13:64, and the corresponding weights of water absorbed (*26*) were determined on 15-mm-wide strips cut at 45° to the machine direction.

Since it was difficult to measure suction height when there was a gradient of hydrophobation through the paper, the edge suction weight is usually reported. Data points in Figs. 2-10 and 8-10 refer to an average of 3 Cobb values or 10 contact angles. Data in Figs. 7-11 refer to single Cobb values. Values for suction weight and wet strength are the averages of at least 4 strips.

Results and discussion

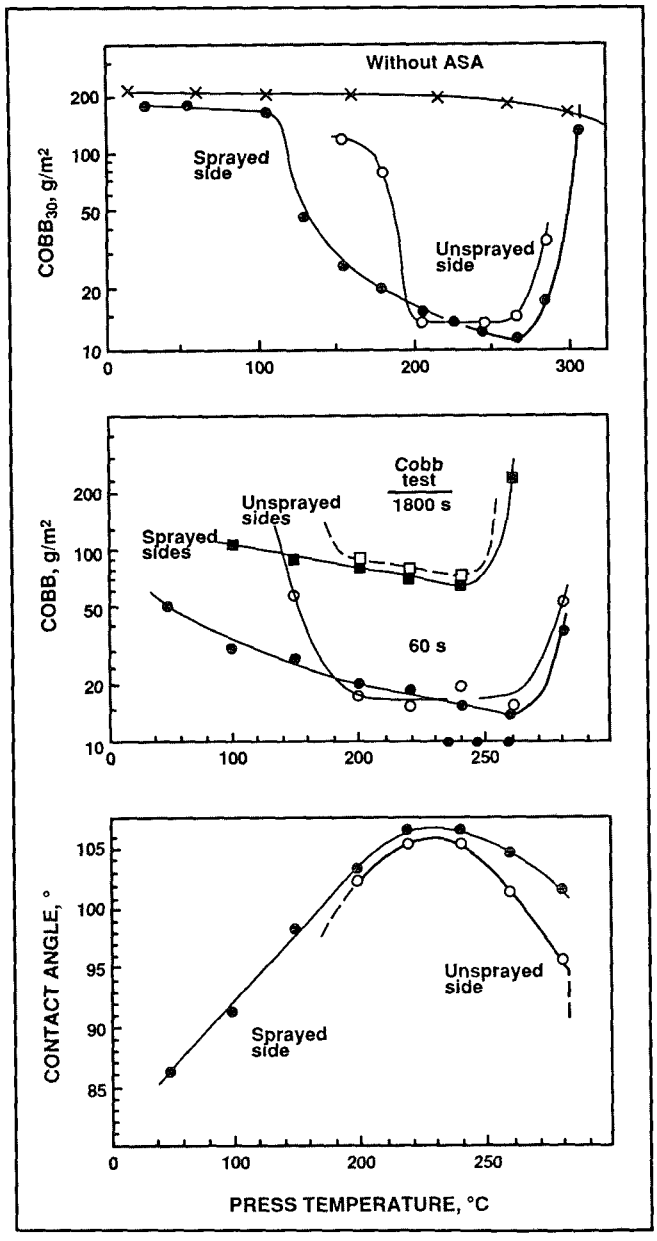
Results with ASA in a 100-ms nip of 0.4 MPa

As mentioned, Fig. 1 illustrates the auto-crosslinking reactions in paper polymers, which occurs whether ASA is added or not. In the first experiment, ASA was applied as a commercial aqueous dispersion stabilized with cationic starch onto the wire side of the unsized laminate paper. A two-sided hot nip of 100 ms and 0.4 MPa was used over a range of press platen temperatures up to 300°C. (Also shown are data for the nip at 200 ms and 4 kPa and data for the dispersion-sized kraft linerboard.)

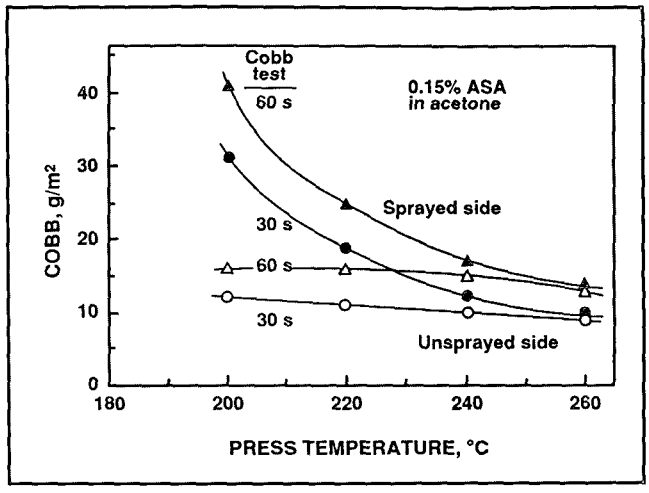
The data on the left side of **Fig. 2** pertain to the sprayed side at three levels of addition (as percentages of paper weight) and a blank without ASA. The $Cobb_{30}$ value is given on a logarithmic scale. The top and bottom graphs on the right side present the corresponding data for the sprayed side when ASA was applied diluted with acetone.

Figure 3 presents data on both the sprayed and unsprayed sides when 0.06% of ASA was sprayed with 40% by weight of acetone. In this nip and for this grammage of 162 g/m², a temperature on both sides of about 230-260°C provides a good redistribution of the ASA throughout the paper. It gives a $Cobb_{60}$ value of 14 g/m² on both sides, although only 0.06% of active ASA was applied only on one side of the paper. At higher temperatures, ASA is either degraded or insufficiently condensed within the paper; thus, it disappears when the paper leaves the press nip. The static contact angle indicates

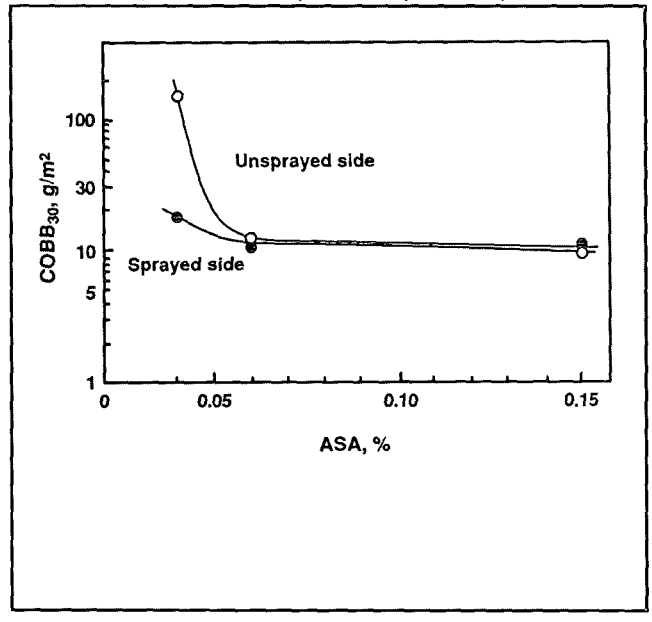
3. The effect of a 0.1-s, 0.4-MPa, two-sided hot nip on the water repellency of an unsized laminate paper sprayed with 0.06% of ASA diluted with 40% acetone. [Data are given as filled symbols for the sprayed side and as open symbols for the the unsprayed back side. Cobb 1800 s refers to 30 min of water absorption, a specialty test for transocean shipping (25).]



4. The effect of a 0.1-s, 0.4-MPa, two-sided hot nip on the water repellency of an unsized laminate paper sprayed with 0.15% of ASA diluted with 20% acetone. Over this limited temperature range, the unsprayed back side has become more hydrophobic than the sprayed side.



5. The water repellency as $Cobb_{30}$ value vs. applied amount of ASA added (sprayed diluted with acetone). Data for both paper sides in 0.1-s, 0.4-MPa, two-sided hot nip of 250°C platen temperature.



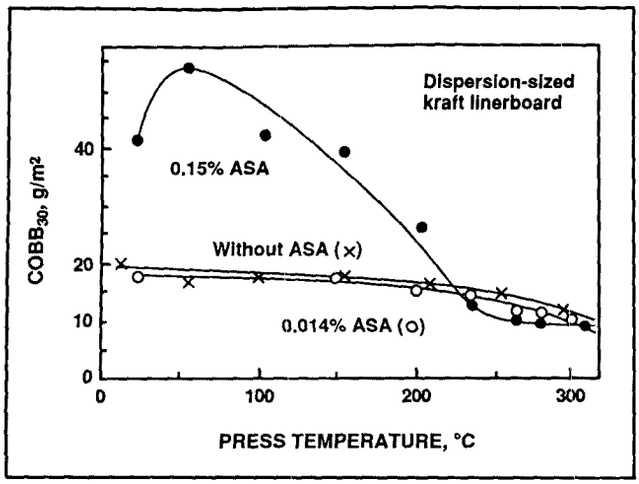
that a press temperature of 230°C is best in regard to the surface layers, giving an angle of about 106°. The $Cobb_{1800}$ value (that is, for 30 min, or 1800 s of water contact) refers to the water absorption for paper plus blotter clamped in below the paper, being a commercial specialty test for linerboard for transocean shipping of boxes. The value of 70 g/m² reached in Fig. 3 is well below the international maximum specification for such linerboard. It is in the same range as that achievable by autocrosslinking of a dispersion-sized linerboard with hot air at a web exit temperature of about 250°C (*4*).

Similar data using 0.15% ASA with only 20% acetone, resulting in slightly larger droplets, are represented in **Fig. 4**. Here, with more ASA available, the unsprayed side of the paper developed better water repellency than the sprayed side. Data over the range of added ASA at 250°C are summarized in **Fig. 5**.

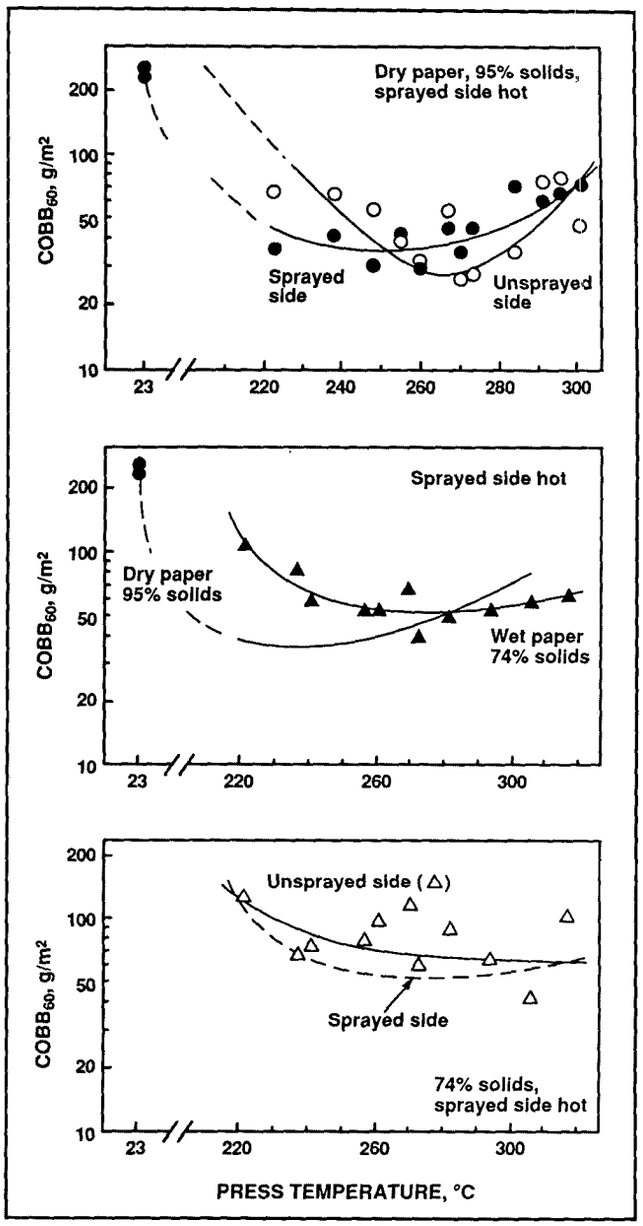
When the water resistance of the sprayed side and that of the unsprayed reverse side are compared in these figures, it appears that conditions can be selected in which the sprayed side develops excellent water repellency, whereas the back side of the paper is rather water absorbent.

Comparing the graphs in Fig. 2, we observe that it is more efficient to apply ASA as an active substance than as a cationic-starch-stabilized

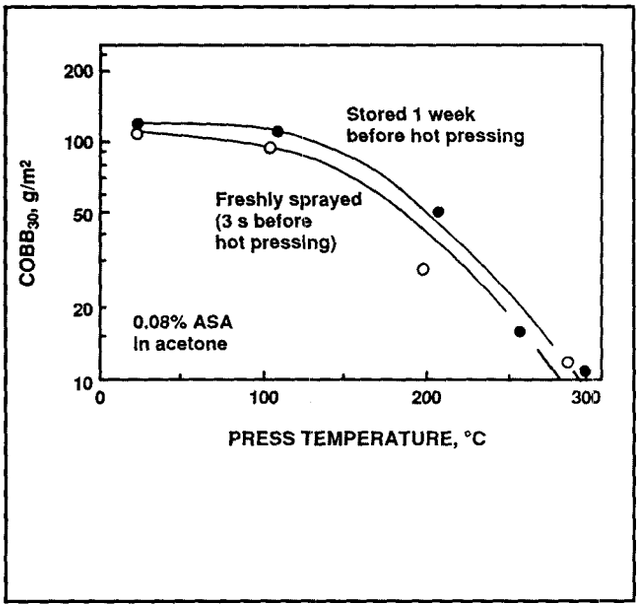
6. The effect of a 0.1-s, 0.4-MPa, two-sided hot nip on the water repellency of a kraft linerboard already dispersion sized, after spraying aqueous dispersions of ASA on one side of the web. Data refer to the sprayed side.



7. The effect of a 0.1-s, 0.4-MPa single-sided hot nip on the water repellency of an unsized laminate paper, sprayed with 0.1% ASA diluted with 20% acetone on the side being heated in the nip



8. The effect of a 0.1-s, 0.4-MPa, two-sided hot nip on the water repellency of laminate papers sprayed with 0.08% ASA with 30% acetone



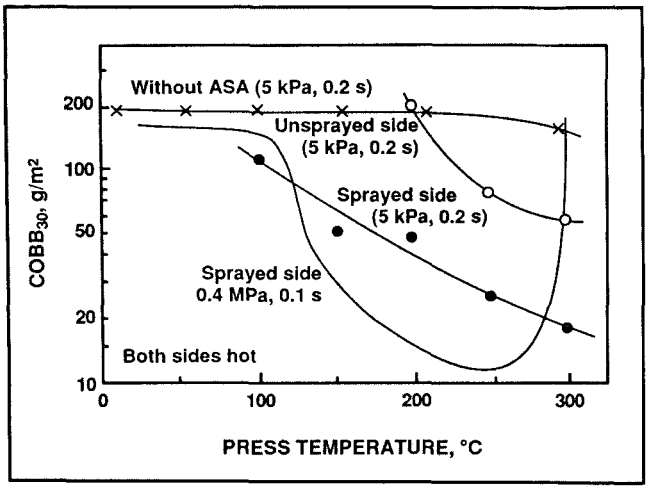
water dispersion. One difference is in the in-going paper moisture content to the nip, which was 5-6% in the case of application as an active substance and 15% for the dispersion. The other difference in these cases is the cationic starch, which was in amount about 2/3 of the amount of ASA.

Figure 6 presents results for aqueous dispersion application to a sized 150-g/m² linerboard (containing 0.08% dispersion size, giving initial $Cobb_{30}$ values of 20 g/m²). With 0.15% ASA but not with 0.014% ASA, some water absorptivity is lost at low nip temperatures but is regained at hot nip temperature of 260-300°C.

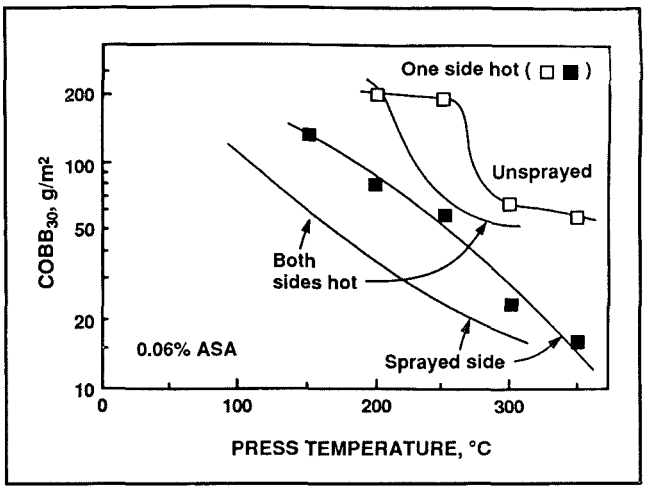
In a later phase, experiments were carried out using a spray with larger droplets, and a slightly larger scatter was observed. The results in **Fig. 7** refer to a single-sided hot nip used with dry, conditioned, and moist paper webs. The laminate paper had been immersed in water for a day and was pressed between blotters to achieve a solids content of 74% in the case of the moist web, in which the web temperature at a given press temperature is presumably lower as a result of heat consumed for water evaporation. The 0.1% ASA was sprayed with additional acetone on the side of the web that was against the hot plate in the nip. At 240-280°C, $Cobb_{60}$ values of 23-27 g/m² were obtained for dry webs with this single-sided hot nip. For the moist web, a $Cobb_{60}$ value of 40-60 g/m² was achieved on the cold side. On the hot side, a $Cobb_{60}$ value of 40 g/m² was achieved, with the press platen temperature being about 300°C.

Figure 8 shows that, although hydrophobation required somewhat

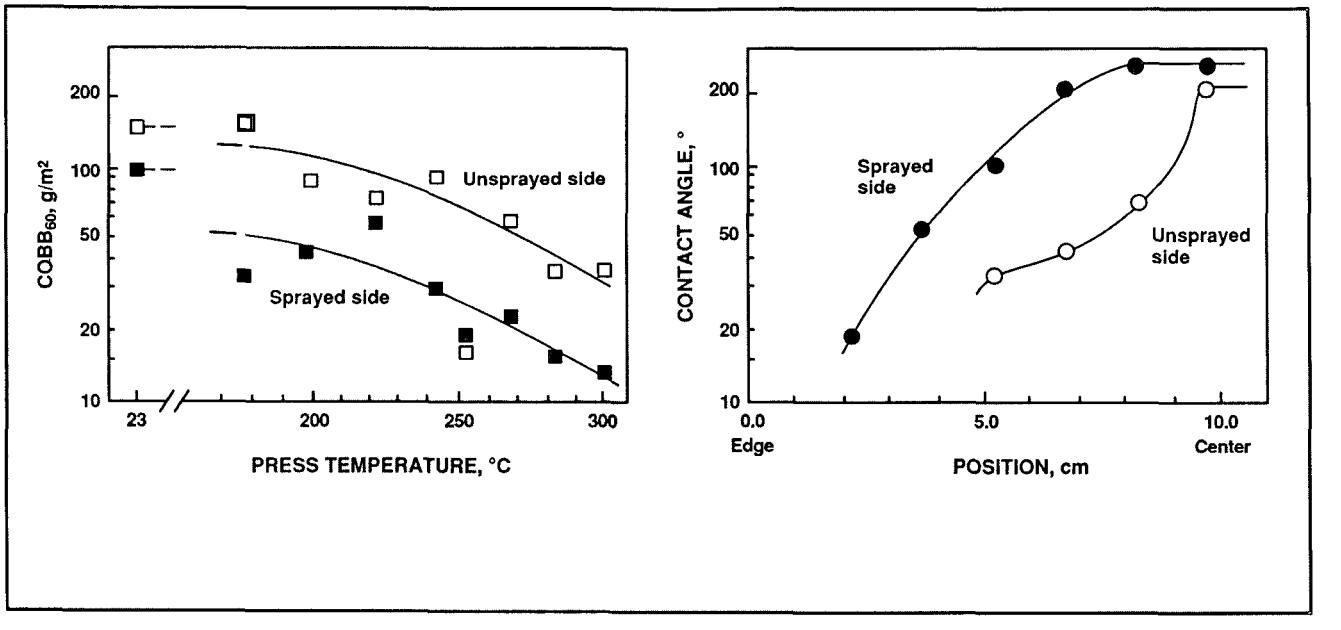
9. The effect of two different two-side hot nips on the water repellency of a laminate paper sprayed on one side with 0.06% of ASA with 40% acetone



10. The effect of 0.2-s, 5-kPa single-side hot and two-side hot extended nips. (The sprayed side is against the hot side of the one-side hot nip.)



11. The effect of the 0.1-s, 0.4-MPa, single-sided hot extended nip on the water repellency of a laminate paper sprayed on the hot nip side with 0.08% AKD as 9% acetone solution. The contact angle for a 300°C platen temperature varied somewhat across the width of the sheet, indicating an uneven spray pattern.



higher temperatures after one week of storage than with a delay of only 3 s after spray application, a gas-phase redistribution was still possible but somewhat less effective. This was the case whether ASA was applied as an aqueous dispersion or in acetone.

Results with ASA in other press nips

When a pressure of only 5 kPa was used and the nip dwell time was extended to 200 ms, a similar hydrophobation was achievable at higher press platen temperatures when both platens were hot, as shown in **Fig. 9**. For the unsprayed side, a nip temperature of 300°C was insufficient. Thus, the contact angle of water on paper treated at 300°C platen temperature was 104° on the sprayed side and 91° on the unsprayed side. The effect may be partly or wholly due to the lower rate of heat transfer at lower nip pressure.

If only one platen was heated, good water repellency on this sprayed side was achieved first at a platen temperature of 350°C, as shown in **Fig. 10**. The contact angle achieved was 108°. Heating both sides of the nip is preferable but not absolutely necessary. A larger amount of ASA, 0.15%, was not an advantage.

At a pressure of 2.5 MPa, with only one press platen hot, the redistribution of ASA was incomplete but was measurable at dwell times up to 22 ms even at 450°C. With 0.10% ASA in acetone, a $Cobb_{30}$ value of 57 g/m^2 and a contact angle of 93° were achieved on the heated sprayed side.

Exploratory experiments have been conducted using the Pira (*21*) pilot rig with a gas-fired cylinder and

a steel band, pressing a dense felt against this cylinder at 0.3 MPa in a 0.3-m-long zone, with a few milliseconds of dwell time in the press roll nip. These experiments indicated that ASA redistribution started at 250°C at a speed of 100-300 m/min. In this case, the cold side of the laminate paper was sealed with an aluminum foil backed by the felt.

Gas-phase hydrophobation with AKD

Figure 11 shows results obtained by spraying 0.08% of a commercial AKD on the web as 9% solution in acetone. The sprayed side was applied against the hot platen in a 0.4-MPa, 100-ms, single-sided hot nip. The reverse side was cold at 20°C. Some water repellency was achieved even at a low press temperature due to good distribution with this dilute AKD solution.

A $Cobb_{60}$ value of about 13 g/m^2 was achieved on the sprayed heated side at a platen temperature of 300°C, and a value of about 40 g/m^2 was achieved on the unsprayed, cold side. The contact angle at this temperature varied across the width of the sheet, which indicated some nonuniform spray distribution of AKD.

Conclusions

An extended hot nip is useful as a self-sealing pressure vessel—that is, as a reactor for gas-phase modification of paper at paper machine speeds or paper converting speeds. Appropriate temperatures range up to 350°C in single-sided or double-sided hot nips, pressures range from a few kilopascals to a few megapascals, and appropriate nip dwell times range from 70 ms to 200 ms.

An excellent gas-phase hydrophobation was demonstrated with small amounts of ASA and AKD sprayed to one side of the web. Various conditions for the extended hot press nip were used for redistribution; in each case, the nip temperature was used as the monitoring variable. The most suitable temperatures will vary with the thickness and basis weight of the paper. Using different temperatures on both sides of the web, a one-sided hydrophobation can be promoted with a temperature gradient through the web.

These gas-phase reactions can take place not only under dry conditions but also in moist webs, such as at 85% or at 74% solids content, as might be found in a breaker stack in a paper machine. A requirement is that web delamination be prevented. The gas-phase reactions in hot-extended nips can presumably be combined with a smoothing of the paper, as in a hot calendering treatment. They are also combined with an auto-crosslinking within the paper web, producing wet strength.

Security problems, ventilation and recovery of unreacted chemicals must be considered. Due to the evaporation of some moisture, the web temperature drops to 90°C at the nip exit. A number of variables within the paper itself may influence the reaction rates. It might be useful to evaluate the effects of repeated hot extended nips, such as with alternative sides against the hot roll. It might also be interesting to examine the effects of extended nips with a band around gas-fired cylinders—for example, a plastic belt or felt with a dense, metallized surface.

It has not been possible to specify minimum nip dwell times necessary. For single-side hot nips, a dwell time of 20 ms even at 450°C was insufficient to achieve reasonable redistribution of ASA through the web. Actual web temperatures and temperature gradients through the web at the nip dwell times used were not measured. [For calculations of web temperatures, see elsewhere (*6, 27*)].

Hot extended press nips could be useful for other types of reactions, such as crosslinking with aldehydes or with di-isocyanates or reactions with phenolic resin or redistribution of fire retardants. Auto-crosslinking is a common simultaneous reaction at 250°C and higher temperatures.

The excellent gas-phase hydrophobation achievable in this procedure would be of interest for various specialty papers, such as those of lower basis weight. For these papers, two-sided hydrophobation might be achievable at shorter nip dwell times or lower press temperatures than presented here for a 160-g/m^2 paper. For offset printing papers or papers to be coated, these hot nips could be useful for improved hydrophobation, even with ASA added to the stock of the machine sheet.□

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