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Borates as Infrared Drying Agents and Bulking Agents in Paper Coatings

Balarama K. Morla
Western Michigan University

BORATES AS INFRARED DRYING AGENTS AND BULKING AGENTS IN PAPER COATINGS

by

Balarama K. Morla

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Balarama K Morla

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Balarama K Morla, M.S.

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In the paper industry, the drying process is the second most energy consuming process after the pulping process; it accounts for around 35% of the total energy consumption. If energy consumption in the drying process can be reduced, the cost of paper production would be decreased considerably. The more recent and wide acceptance of the use of infrared energy for the drying of coated grades has led to many developments and improvements in materials and controls, making IR a practical and safe method for the paper industry. This process is mainly based on the absorption of infrared radiation by paper coatings. IR drying directly affects both the time of drying and the rate of drying. With infrared drying, the time of drying can be reduced, which directly influences the economics of the paper production.

In this study, we tried to study the borates as borates absorb the infrared radiation at a maximum level at wavelengths of 2-3 μm, which is similar to water absorbency. The objective of this study was to investigate the influence of borates on the infrared drying of paper coatings. Also at the same time the bulking effect of Borates on paper coatings was studied.

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CHAPTER I

INTRODUCTION

Coated papers and boards are used in almost all facets of our lives, especially in printed media and marketing communications. Demand for and capacity to make coated papers have grown rapidly, largely driven by technological improvements in printing processes. In search of improved profitability and quality, many producers of coated papers are increasing their focus on differentiating their products from their competitors.

The improper drying of coated paper or coated paperboard can be disastrous to the quality of finished product. The main objective when drying coated paper is to allow optimum penetration of the coating into the paper, while avoiding migration of the pigment or adhesive particles since this can cause mottle. Water makes up 25% to 50% of a coating formulation, and the excess must be dried quickly and efficiently. The quality parameters that are affected by drying are mottling, gloss, smoothness, printed gloss, and surface strength.

To overcome the above problems, most mills have been using infrared drying over the last three decades. The non-contact characteristic makes IR ideal for pre-heating and initial drying of wet coating before it comes into contact with cylinders. Apart from quality of the product, small space demands and good controllability also favor infrared drying. The radiation efficiency of an electrical radiator is 80-85%; this is defined as that part of electrical energy transformed to radiation at infrared wavelengths. Drying efficiency, the part of electrical energy that is consumed in the heating of the web or in the evaporation of water, is 25% to 45%.[1]

Efficiency of the drying can be increased by a back reflector, decreasing the distance between radiator and the web, keeping the protective glass clean, or optimizing the amount of cooling air.[2]

By increasing the absorbency of the IR radiation, the speed of drying increases and results in higher productivity. In coating colors, water is transparent to infrared energy, so it absorbs the energy and is heated. Addition of infrared absorbing compounds in coating colors improves the absorbency of the radiation, which could result in a higher drying efficiency. If IR absorbing compounds are used in paper coatings, this will absorb IR radiation and the paper coating will dry quickly. At the same time, the additives must be compatible with the other coating color components, and they should not affect the quality of the coated paper. Today, the market demands improved overall performance of the finished, printed coated paper. High quality coated paper requires higher brightness, opacity, gloss and good printability without sacrificing runnability or economics. In respect to paperboard, good coverage or hiding power of the coating is essential.

CHAPTER II

LITERATURE REVIEW

Infrared radiation

The drying of the coated paper web is a very complicated process. Just getting the paper dry is not enough; one has to know the ideal method of water removal to achieve the required paper quality. A required characteristic for coating dryers is the fact that the initial stage of drying has to take place without contact with the paper web, since wet coating does not allow mechanical contact. Traditional methods of coating drying are flotation dryers, IR dryers, and steam heated cylinder dryers. The non-contact characteristic makes IR ideal for pre-heating and initial drying of wet coating before it comes in contact with the steam cylinder dryers. Fast controllability of the infrared dryers compared to air and cylinder dryers eases startup after web brakes and grade changes.

Infrared energy is radiated from any object or material that is warmer than its environment. Infrared heat transfer occurs when two objects at different temperatures are in proximity of each other. IR radiation, whether generated from an electric or a gas system, is emitted by atomic excitation of any substance. The IR energy travels in the form of electromagnetic waves at the speed of light, even through a vacuum, until it strikes another substance where it may be absorbed, reflected, or transmitted. Radiation utilizes the electromagnetic energy from the heat source to transfer its energy to the object being heated. Infrared radiant energy is not absorbed by air, and does not actually become heat until it is absorbed by an opaque object. Radiant energy may appear as heat as it vibrates and rotates the atoms on the absorbing object, which results in a rise in temperature of the object. Electromagnetic waves occur over

a range of wavelengths, from 10^{-16} μm to 10^{6} μm, with IR energy falling in the "invisible light" range between 0.7 μm to 100 μm. The useful wavelengths for industrial applications are from 1-10 microns, because absorption of many materials in the 3-8 micron range is especially effective. [3]

There are several physical laws that explain the properties of infrared radiation. The first and probably most important of these laws states that there is a positive relationship between radiant efficiency and the temperature of an infrared source. The proportion of energy transmitted from a heat source by each of the three heat source methods is dependent on the physical and ambient characteristics surrounding the heat source, and, in particular, the source's temperature.

The Stefan-Boltzman Law of Radiation states that as the temperature of a heat source is increased, the radiant output increases to the fourth power of its temperature. The conduction and convection components increase only in direct proportion with the temperature changes. Thus, as the temperature of a heat source is increased, a much greater percentage of the total energy output is converted into radiant energy.

The general equation for infrared heat transfer is as follows[2]:

$$\mathbf{Q/A = Fv * e_s * a_t * s * (Ts^4 - Tt^4)}$$

Q/A = Infrared heat transfer (W/cm^2)

Fv = Geometric view factor (0 - 1)

e_s = Emissivity of the source (0 - 1)

a_t= Absorptivity of the target (0 - 1)

s = Stefan-Boltzmann Constant, $5.670* 10^{-8}$ $W\ m^{-2}\ K^{-4}$

T_S= Source temperature (K)

T_t= Target temperature (K)

The wavelength of infrared radiation is dependent upon the temperature of the heat source. A source temperature of 3600 °F will produce a short wave of approximately 1 μm, while a source temperature of 1000 °F will produce a longwave of approximately 3.6 μm. The wavelength dramatically impacts the intensity of radiation at the subject. A critical function of the wavelength of infrared radiation is its ability to penetrate an object. The penetration of infrared energy is a function of its wavelength. The higher the temperature, the shorter the wavelength. The shorter the wavelength, the greater its penetrating power. For example, a tungsten filament quartz lamp operating at 4000 °F has a greater ability to penetrate into a product than a nickel chrome filament quartz tube operating at 1800 °F. There are certain advantages gained in industrial processing by using the penetrating capabilities of short wave infrared.

Infrared emitter	Temp (°C)	Temp (°K)	Wave length range, maximum of emission
Long wave	Up to 800	Up to 1050	Up to 2.7
Medium wave/carbon	800 up to 1300	1050 up to 1600	2.7 up to 1.85
Fast medium wave	1500 up to 1800	1800 up to 2100	1.6 up to 1.4
Short wave	1850 up to 2350	2150 up to 2600	1.4 up to 1.2
Near IR	2350 up to 3000	2600 up to 3300	1.2 up to .88
Visible light	3400 up to 7300	3700 up to 7600	.78 up to .38

Table 1: Infrared temperature and wave length range[3]

The characteristics of the paper web define how large a portion of the radiation is absorbing into the web. Water has two absorption maximums at wavelengths of 2.95 and 6.1 μm, and the fibers absorb radiation best with wavelengths between 3 and 8 micrometers. Shorter wavelengths (0.75 – 2 μm) are transmitted through the web or reflected from the surface, yet partly absorbed by the web. The basis weight of the web is one factor affecting the efficiency of the radiator and the proportion of the total energy, which is absorbed by the web.[2]

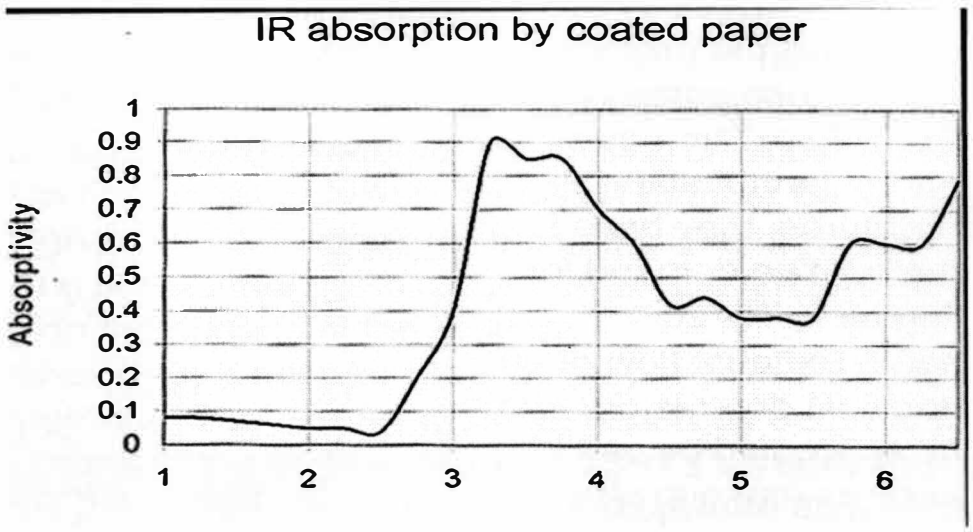

Figure 1: Spectral properties of a coated LWC paper[12]

Infrared dryers

Infrared dryers are widely used in the paper industry, mainly for drying of coated paper and correcting moisture profiles. IR dryers are small units with very high heat flux, which makes them easy to retrofit on existing machines. The heat flux is obtained with out contact, which is a major advantage in drying of coated paper. Two types of IR dryers are widely used in the paper industry, gas fired medium wave dryers and electrically heated short wave dryers. These two dryers types are quite different in design and operating principle.

The radiation efficiency of an IR heater is the fraction of supplied energy, fuel or electricity that is actually converted into radiation. The radiation efficiency can be thought of as an upper limit for the efficiency of the heater working in a dryer. Losses of radiation are inevitable, and energy not converted into radiation is normally used only to a small extent in the dryers. The fraction of supplied power that actually ends up in the paper depends on the radiation efficiency of the IR heater and the paper quality.[4]

The Lambert- Bouger law gives the amount of radiation absorbed by the paper web,

$$q_{abs} = q_{rad} (1 - e^{-C\mu.\delta})$$

q_{rad} = the flux of infrared radiation exposed on to the web

q_{abs} = the heat flux absorbed in the web

C_α = absorbtivity per thickness unit

δ = the web thickness

A typical radiation source for an electric IR dryer is a 2 or 3 KW halogen lamp, producing short-wave infrared radiation with a filament temperature of around 2200 °C; it emits both short and medium wave thermal radiation. Infrared radiation can penetrate in to web. It absorbs gradually while passing through the web. The medium waves are absorbed by the water and fiber, while the short waves penetrate deeper in to the web. The IR lamp is equipped with a reflector, of which there are two basic types: a mirror reflector and a heat absorber, "hot back wall" (usually a ceramic material). The mirror surface reflects the heat directly back and through the protective quartz glass in front of the lamps. The heat absorber partly reflects heat and partly absorbs the heat in the ceramic material, which then starts operating as a medium-wave radiator. A standard for all of these electric IR units is a protective quartz glass. This is placed between the IR lamps and the paper web to protect the internals of the emitter from dirt and to close the cooling air circulation so that it does not disturb the paper web. With sheet weights up to 150 to 180 g/m^2, the coating can be dried by placing the IR modules on the uncoated side of the web. With low sheet weights, the short-wave radiation partly passes through the web, and therefore it is necessary to use a reflector or co-radiator. In order to ensure runnability, electric infrared dryers used for coating drying are usually of a closed frame type, and no air is allowed to blow against the sheet. In the drying of heavier board grades, there is an option to

apply air to the sheet to speed up evaporation by allowing moisture saturated air to be pushed away from the sheet surface.[5]

When the web exits the coating unit, its temperature is usually 20 to 40° C lower than what is required for efficient evaporation. Raising the temperature of the web to the evaporation temperature requires a lot of energy, especially with fast and wide machines. When the web temperature has reached 65 to 85 °C, evaporation is strong, and most of the energy is consumed by the evaporation process, although the sheet temperature is still gradually increased. It is important to note that one of the key purposes of an IR dryer is to load drying energy into the web. How this energy is then released as evaporation depends on the dryers and the web draws following the IR dryer. Raising the temperature with IR, followed by an air dryer, is considered the most efficient and best performing coating drying method.[1]

Borates

Polyatomic ions exhibit characteristic infrared spectra. When a beam of electromagnetic radiation is passed through a substance, it can either be absorbed or transmitted depending upon its frequency, and the structure of the molecule it encounters. When a molecule absorbs radiation, it gains energy as it undergoes a quantum transition from one energy state to another. If the transition is from one vibrational level to another, then the radiation is from the infrared portion of the electromagnetic spectrum and it is known as Infrared Spectroscopy. If a crystal is composed of mono-atomic ions, such as sodium chloride, the only vibrations are lattice vibrations in which the individual ions undergo translatory oscillations. The corresponding spectral bonds are broad and are responsible for the long wavelength cutoff in transmission. In a crystal containing polyatomic ions such as ammonium chloride, the lattice vibrations also include rotatory oscillations.[6]

The characteristics of the paper web define how large a portion of the radiation is absorbed to in the web. Water has two absorption maxima at wavelengths of 2.95 and 6.1 μm, and the fibers absorb radiation best with wavelengths between 3 and 8 micrometers. Shorter wavelengths (0.75 – 2 μm) are transmitted through the web or reflected from the surface, yet partly absorbed by the web.[2] From table 2, we can see borates absorb IR radiation in the wavelength range of 2-3 μm very strongly. Thus if borates are present in the coating formulations, they will absorb the infrared radiation along with water during the drying process which may potentially increase the drying rate.

Compound	Formula	Wavelength, μm
Sodium metaborate	$NaBO_2$	2.85, 10.80, 7.64
Magnesium metaborate	$Mg(BO_2)_2.8H_2O$	9.2, 8.8, 2.98, 2.86
Lead metaborate	$Pb(BO_2)_2.H_2O$	10.3
Sodium tetraborate	$Na_2B_4O_7.10H_2O$	7.35, 7.05, 3.0
Sodium perborate	$NaBO_3.4H_2O$	10.7, 3.0
Potassium tetraborate	$K_2B_4O_7.5H_2O$	10.0, 3.03, 2.95, 2.81
Boric acid	H_3BO_3	6.9, 3.15

Table 2: IR absorption wavelengths of borates[6]

In this study Sodium Tetraborate Pentahydrate and Di Sodium Octaborate Tetrahydrate were selected as the additives in the coating formulations. The absorption wavelengths are not available for these borates, so by using diffusive reflectance method infrared spectroscopy of Neobor, Polybor and Borax were studied.

Neobor and Borax are both hydrated forms of disodium tetraborate, $Na_2B_4O_7$. The borate anion is exactly the same in crystals of Neobor and Borax. It can be written as $[B_4(OH)_4O_5]^{-2}$ to assist understanding its structure. Neobor crystallizes from solutions of the appropriate concentrations and Na_2O: B2O3 mole ratio at temperatures above 60.8^0C. Borax is the stable crystalline phase in equilibrium with solutions below this temperature. Polybor is an amorphous mixture, and does not have a structure.

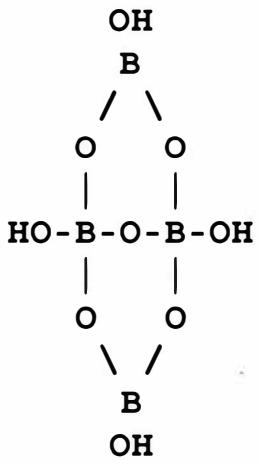

Figure 2. Structure of borate anion in Neobor

Borate minerals (BO_3) are capable of polymerization in the form of chains, sheets, and isolated multiple groups. This is possible because the small B^{3+} ion, which generally coordinates three oxygens in a triangular group, has bond strengths to each O exactly half the bonding energy of the oxygen ion. This permits a single oxygen to be shared between two boron ions linking the BO_3 triangles into expanded structural units (double triangles, triple rings, sheets, and chains). Because the triangular coordination of BO_3 is close to the upper stability limit of 3-coordination, boron is found also in 4-coordination in tetrahedral groups. In addition to BO_3 and BO_4 groups, natural borates may contain complex ionic groups. In borax, a complex ion consisting of two tetrahedral and two triangles is found.

The fundamental building block of borates is a boron ion surrounded by three Oxygen ions in the same plane, $(BO_3)^{3-}$. In the aqueous borate coatings, there will be a number of borate anions in equilibrium. The nature and proportions of these anions are governed by the temperature, pH, Na_2O: B_2O_3 ratio, and overall concentration of Na_2O and B_2O_3. The $[B_4(OH)_4O_5]^{-2}$ ion is an important anion in aqueous solution but is never the only anion present. At low pH (less than 6), $B(OH)_3$ will be present at nearly 100%. At high pH (above 12) the tetrahedral metaborate $[B(OH)_4]^-$ will be essentially the only anion present.[7]

There are many applications of borates in the paper industry. Newly developed borate autocausticizing technology, has demonstrated that borates react with a portion of the sodium carbonate in the recovery boiler to form a borate compound. When hydrated in the smelt dissolving tank, these borate compounds convert to sodium hydroxide. The process reduces lime and energy requirements, decreases lime mud disposal, and requires little or no capital investment to implement. Neobor is part of the starch adhesive formulation for corrugated paper and paperboard, and is a peptizing agent in the manufacture of casein based and dextrin based adhesives. It greatly improves the tack and green strength of the adhesive by cross linking conjugated hydroxyl groups.[8] Previous rheological studies on borates with clay, carbonate, and latex systems indicated that borates are very compatible with coating pigments and binders.[9]

Bulking in paper coating applications

Brightness and opacity are two primary characteristics of paper and are the most important reflectance values of paper. Both have been the targets of intense investigation throughout the years. These optical properties have a significant impact on printed paper properties. Paper opacity is an important attribute and is one of the key quality measurements. The utility of bond, writing, and book papers is enhanced by a high opacity.

Researchers have found that extensive bleaching raises brightness, but has a negative effect on opacity. Increasing the opacity without impacting other properties like strength, shade, sizing, or brightness is a concern of every paper maker. Inorganic additives like clay, calcium carbonate, talc, and titanium dioxide have been added to the fiber mix to increase brightness and opacity. High bulk fibers, like ground wood and TMP, are used to increase opacity in some grades of paper. However, brightness

and brightness reversion complicate their use as an opacifier in high brightness papers.[10]

Fillers are being used more often in board applications such as mottle and solid linerboard for increased brightness and coverage. These grades are made of multiple plies: the inner ply consisting of low brightness, unbleached kraft or recycled fiber, and the top ply of unbleached pulp, which can contain filler. Board products are primarily used as containers or cartons, and strength is a critical factor. Increased loading increases opacity, but due to the loss of strength seen with filler usage in the top ply, loading levels are limited.[11] The best product is defined as the sample exhibiting the highest brightness and coverage. Paper quality depends on the coverage. Coverage indicates how well the coating is able to hide the base paper under it. Coverage, in this application, is a function of opacity. However, since the opacity of board products is always 100, coverage is best quantified by brightness gain and top ply consistency over the unfilled board.[12]

Opacity of a paper can be expressed as an almost linear function of the product of its light scattering coefficient and grammage (basis weight). Light scatters from optical surfaces; thus the light-scattering power of paper depends on the number of optical surfaces. Refining pulp fibers improves sheet tensile strength while decreasing printing opacity. Opacity decreases with increased beating because the increase in the inter-fiber bonded area leaves less fiber area interface available to scatter light. Raw stock opacity substantially affects final opacity.[12]

Opacity represents a substrate's light blocking ability. It is the opposite of transparency. Opacity characterizes the ability of paper to hide text or pictures on the backside of the sheet. Opacity is important for writing and printing papers generally, and particularly for thin printing papers, so as to avoid show-through. When the basis weight of the paper decreases, its opacity undesirably reduces. Higher opacity values allow better readability on one side, because the print showing through from the other

side is less noticeable. The utility of bond, writing, and book papers is enhanced by a high opacity.

Opacity is a fundamental optical property of paper as a whole, yet the measurement of opacity is determined by a ratio of reflectance measurements. Opacity is a measure of the amount of light transmitted through the paper. When no light is transmitted, the opacity is 100%. The essential principle of this method for determining the opacity, the reflectance of paper when combined with a white backing, is higher than that of paper when combined with a black backing. This is because, in the former case, light transmitted through the imperfectly opaque sheet is largely reflected by the white backing, and a portion of the light is transmitted through the paper a second time thus increasing the total reflection. Opacity increases with increased absorption and scattering of light.

Opacity (89% reflectance backing) is sometimes called contrast ratio. $C_{0.89}$ is defined as 100 times the ratio of the diffuse reflectance, R_0, of a specimen backed by a black body of 0.5% reflectance or less to the diffuse reflectance, $R_{0.89}$, of the same specimen backed with a white body having an absolute reflectance of 89%. Thus,

$$C_{0.89} = 100*(R_0/R_{0.89}).$$

Accordingly, the contrast ratio is 100% for perfectly opaque paper and is only a few percent for perfectly transparent sheets.

Opacity (paper backing), sometimes called printing opacity, is defined as 100 times the ratio of the light reflected by a paper specimen when the specimen is backed by a black body of 0.5% reflectance or less, R_0, to that when the specimen is backed by a thick stack of the same kind of paper R; thus

$$\text{Opacity (paper backing)} = 100* (R_0/R_\alpha)$$

The opacity of the sheet is influenced by thickness, the amount and kind of filler, degree of bleaching of the fibers, basis weight, coating components, especially the type of coating used, and the degree of calendering.[14]

Most quality coated papers require the use of TiO_2 to achieve the desired opacity at high brightness. The key question is how can a mill maintain or improve its paper quality and optimize TiO_2 use?. Since TiO_2 is more expensive than pulp and other mineral pigments like kaolin clay and calcium carbonate, it is most cost effective to optimize the use of these non-TiO_2 components to achieve the target opacity.[10]

Brightness and opacity are especially important for lightweight, wood-free papers and LWC papers. This is related to the fact that the coat weights are getting lighter; however, a better coverage is necessary to reach the expected goals. LWC papers have a low basis weight and a single coating of 6 – 10 gsm per side. Coat weights are light, so the pigment has to give good coverage of the surface. The coating weight for LWC papers is approximately 30 % total sheet weight; the basis weight ranges from 51 - 65 g/m^2. Even in the case of newsprint, due to the increase of postal rates, technology is shifting towards low coat weights. In board coatings the requirements for surface coverage and print quality are also growing significantly. Recovered paper consumption at paperboard mills is expanding rapidly, and the recycled paperboard grades recorded the highest growth rates over the past several years. In recycled paperboard, bulking is most important to cover the base sheet properties.

The light scattering coefficient is defined as the fraction of light incident upon an infinitesimally thin layer of material that is scattered backwards by that layer, divided by the (infinitesimal) grammage of the layer. Scattering coefficient is expressed in reciprocal grammage units. A multiplier (1,000) is used to convert m^2/g to the standard units, m^2/kg.[14]

The reflectances R_0 and R_α are not the general material properties, but they characterize the paper sheet from which they are measured. The light scattering coefficient is generally used to transform these values to coefficients of light

scattering and absorption in paper.

$$S= (1/W) * (1/[(1/ R_\alpha) - R_\alpha]) * \ln [(1-(R_0* R_\alpha))/(1-(R_0/ R_\alpha))]$$

From the opacity meter, the light scattering coefficient and absorption coefficient of the specimen can be calculated by using T425 om-96. Using R_0, R_α, and W (grammage) in g/m^2,

$$a= 0.5 [(1/ R_\alpha) + R_\alpha]$$

$$b= 0.5 [(1/ R_\alpha) - R_\alpha]$$

$$X= [1-a R_0]/[b R_0]$$

Scattering power, $(sW) = (0.5/b)* \ln [(X+1)/(X-1)]$

Scattering coefficient, $(s) = 1000* sW/W$

CHAPTER III

STATEMENT OF PROBLEM AND OBJECTIVE

Drying is the second most energy consuming process in the paper industry and is the main limiting factor for the increase in production rates. Infrared drying is the modern technology available to the paper industry, and it provides better control with maximum efficiency than other drying methods. Still, drying remains as a limiting factor for maximum attainable production rates.

Increasing the efficiency of the infrared drying increases the rate of drying, consequently increasing productivity. The incorporation of IR absorbing borates in the wet coating was studied to determine, if the IR drying rate could be improved.

The objectives of this research are:

1. To determine if IR absorbing borates improve IR drying rate,
2. To measure the optical properties of coated papers to determine bulking properties, and,
3. To determine if the borates adversely effect the high speed runnability of coatings.

CHAPTER IV

EXPERIMENTAL PLAN

Based on the previous studies, borates were selected as the coating additives for increasing the efficiency of infrared drying. Even through data for some borate salts absorption frequencies was obtained from literature, the data for Borax, Polybor and Neobor are not available. So, initially, the infrared spectra of all the three borates were measured (fig.3). Depending on the solubility data for borates, different coatings were formulated with 1, 2, and 4% borates.[9]

The experimental plan was divided into three phases. In Phase I, the runnability of borates with two pigments (clay and carbonate) on a Cylindrical Laboratory Coater was studied. In Phase II, the optical properties and surface properties of the coated sheets were measured to study the effect of borates on paper properties. In Phase III, drying rates were studied for coatings using the laboratory infrared dryer.

Coating formulations

Since the main objective of this research was to study the use of borates to improve IR drying efficiency of coated papers, the study is confined only to basic coating formulations containing a pigment, a binder, and one of several types of borate products. In 2000, the total paper industry pigment consumption was about 22.3 million tons, according to the PITA Coating Work Group. Of this tonnage, kaolin represented 44%, GCC 35%, PCC 16%, and other pigments 5%. North America's 1995 total coating latex adhesive consumption was 345,000 dry tons with the following market shares: styrene-butadiene 83%, polyvinyl acetate 11%, styrene acrylic 3%, vinyl acrylic 2%, and ethylene vinyl acetate 1%.

Keeping these statistics in mind, the following materials were selected for the coating formulations

Pigment:

Hydrogloss 90 (Huber Engineered Materials)

Hydrocarb 90 (OMYA)

Binder:

Styrene-Butadiene latex (CP 620 NA, Dow Chemicals)

Poly Vinyl Acetate (Polyco 2152, Rohm & Haas Company)

Borates:

Neobor --- Sodium Tetraborate Pentahydrate ($Na_2B_4O_7$. 5 H_2O)

Polybor --- Di Sodium Octaborate Tetrahydrate ($Na_2B_8O_{13}$ .4 H_2O)

The basic formulation is made to 60 % solids

Pigment 100 parts

Binder 10 parts

Borates 1 %, 2 %, or 4 % (based on the amount of water)

For adjustment of viscosity, an alkali swellable thickener (Alcogum) was used, and for adjustment of pH, ammonium hydroxide was used. The above formulations were selected based on the previous studies of solubility rates of borates and rheological properties of the coating formulations.[9]

The order of addition during the formulation preparation was

Pigment dispersion

Borates

Binders

pH adjustment

Viscosity adjustment

Sample calculation for borates

Sample size: 3000 gms

Percent solids: 60

Amount of solids: 1800 gms

Component	Parts (x)	% (x/110 =y)	% of solids (a)	Weight (gms) (y*1800/a)
Pigment	100	90.9	70	2337.42
Binder	10	9.09	50	327.24
Total parts	110			2664.66

Table 3: Sample calculation for formulation of borates

Additional water to be added to the formulation: 3000- 2664.66 = 335.34 gms

	Na_2O	Boron	B_2O_3	H_2O	FW	% B_2O_3	Wt of Boron	% of Boron
Neobor	1	4	2	4.67	285.37	48.79	43.244	15.15
Polybor	1	8	4	4	412.54	67.50	86.488	20.96

Table 4: Boron weight percentage in borates

Phase I

Based up on the high shear rheological measurements from previous data[4], a total of 12 coatings were selected for running on the CLC. For these formulations, the pH was maintained in the range of 8.0 to 8.5, and low shear viscosity was maintained in the range of 600-1000 cp. Viscosity was measured by Brookfield RVT viscometer with # 6 spindle at 100 rpm. For adjustment of viscosity, a alkali swellable thickener (Alcogum) was used, to adjust the low shear viscosity in the range of 600-800 Cps.

Sample Number	Hydrogloss	Hydrocarb	SBR	PVAc	Neobor	Polybor
1	100	0	10	0	0	0
2	100	0	10	0	1	0
3	100	0	10	0	2	0
4	100	0	10	0	0	1
5	100	0	10	0	0	2
6	100	0	10	0	0	4
7	0	100	10	0	0	0
8	0	100	10	0	0	4
9	0	100	10	0	0	1
10	0	100	10	0	2	0
11	100	0	0	10	0	4
12	100	0	0	10	0	0

Table 5: Samples for CLC run

All the above formulations (Table 5) were run on the CLC, using a LWC base sheet of 30 gsm at different coat weights ranging from 3 gsm to 8 gsm.

Phase II

After running the coating formulations on the CLC, the optical properties of the coated substrates (opacity and brightness) were measured. Opacity was measured according to TAPPI test method T 425. Opacity values were used for analyzing the effect of borates as bulking agents. Brightness was measured according to TAPPI test method T 452.

Void fractions of coatings were measured using an oil absorption method.[15] For this coating, at different percentages of borates were applied to Mylar sheets with wire wound rods using the laboratory draw down unit. For all samples, coat weight was adjusted around 20 gsm. Silicone oil was applied on the dry coating layer of known weight and allowed to penetrate. After two minutes excess oil was wiped away with blotting paper and the sample was reweighed. Void fraction value is given by ratio of volume of oil absorbed to the total volume of the dry coating. Light Scattering coefficients are calculated from the opacity meter, using R_0 and R_α measured at same wave length.

Phase III

Based upon the results from Phase II, six coatings were selected for infrared drying studies. Mylar was selected as the substrate, since it offered a uniform basis weight with little deviation.

Hydrogloss + SBR

Hydrogloss + SBR + 2 % Neobor

Hydrogloss + SBR + 4 % Polybor

Hydrocarb + SBR

Hydrocarb + SBR + 2 % Neobor

Hydrocarb + SBR + 4 % Polybor

All the coatings were prepared at 60 % solids, and the mylar coated with a laboratory draw down unit. Higher coat weights were applied to reduce the error in the drying calculations. The coat weight of the samples was adjusted to 25 to 30 gsm. Samples were then dried with the help of laboratory infrared dryer for specific time and specific intensity. Then, the dried samples were further dried with the help of a laboratory microwave. The initial weight and final weight of the sample before and after drying in the microwave were noted, and the percentage change in moisture per unit coat weight was calculated. The same procedure was applied for all the coatings, and percent change in the moistures per unit coat weight were compared with the control to study the effect of borates on IR drying.

CHAPTER V

RESULTS AND DISCUSSIONS

Infrared spectroscopy of borates

From the previous studies it was proven that for carbonate systems, the degree of interaction between borates and carbonate systems decreases in the order of Polybor, Neobor, and, Borax.[4] For clay systems, it decreases in the order of Neobor, Polybor, and Borax. The main objective of this research was to find the influence of borates on the infrared drying. To check their suitability as drying agents, infrared spectroscopy of all three borates was measured using the diffusive reflectance method.

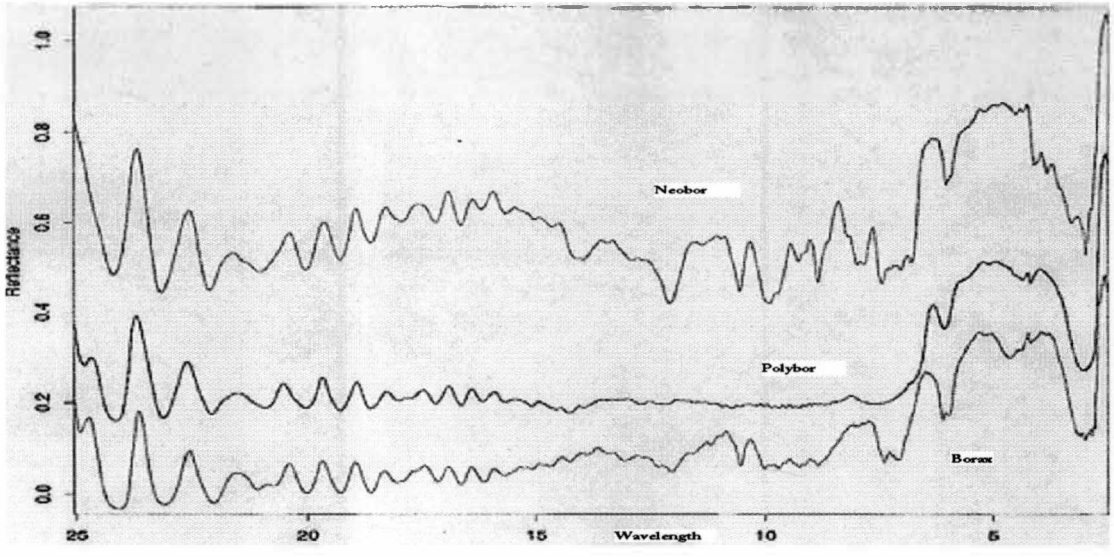

Figure 3: Infrared spectroscopy of borates

From Figure 3, it is observed that all three borates have a maximum absorption frequency in the region of 2 – 2.5 μm. This absorption frequency makes them suitable for application in the drying process because both water and the paper web absorbs the infrared radiation in the same region.

Effect of borates as bulking agents

In Phase I, during preparation of the coatings, it was observed that the coatings with the Polybor were behaving differently from coatings with Borax and Neobor. Polybor coatings had a higher low shear viscosity than the other two coatings at any given percentage weight. However, at high shears, the coating viscosities were similar. Based on the CLC trials, it was observed that coatings with Neobor are had good runnability when compared to coatings with Polybor. At coat weights below 5 gsm, the samples with Polybor coatings did cover well. But, at higher coat weights, there was no such difference between the samples. In CLC trails, it was very difficult to attain the same coat weights for all the coatings.

Even though the effect of borates on infrared drying was the main objective, it is necessary to check the effect of borate coatings on other properties of the coated samples. Even though trials were held for a total of 12 coatings (based on parts of different borates), samples were grouped to five different weight percentages, along with the control sample with 0% of boron.

Sample	HG	HC	Borates	Boron	Borate
1	100	0	0		----
2	100	0	0.43	0.13	Neobor
3	100	0	0.60	0.188	Polybor
4	100	0	0.87	0.27	Neobor
5	100	0	1.33	0.374	Polybor
6	100	0	2.37	0.73	Polybor
7	0	100	0	0	----
8	0	100	0.60	0.188	Polybor
9	0	100	0.87	0.27	Neobor
10	0	100	2.37	0.73	Polybor

Table 6: Formulations in terms of boron percentage

For all the coated samples opacity and brightness values were measured, as these two properties are the main optical properties.

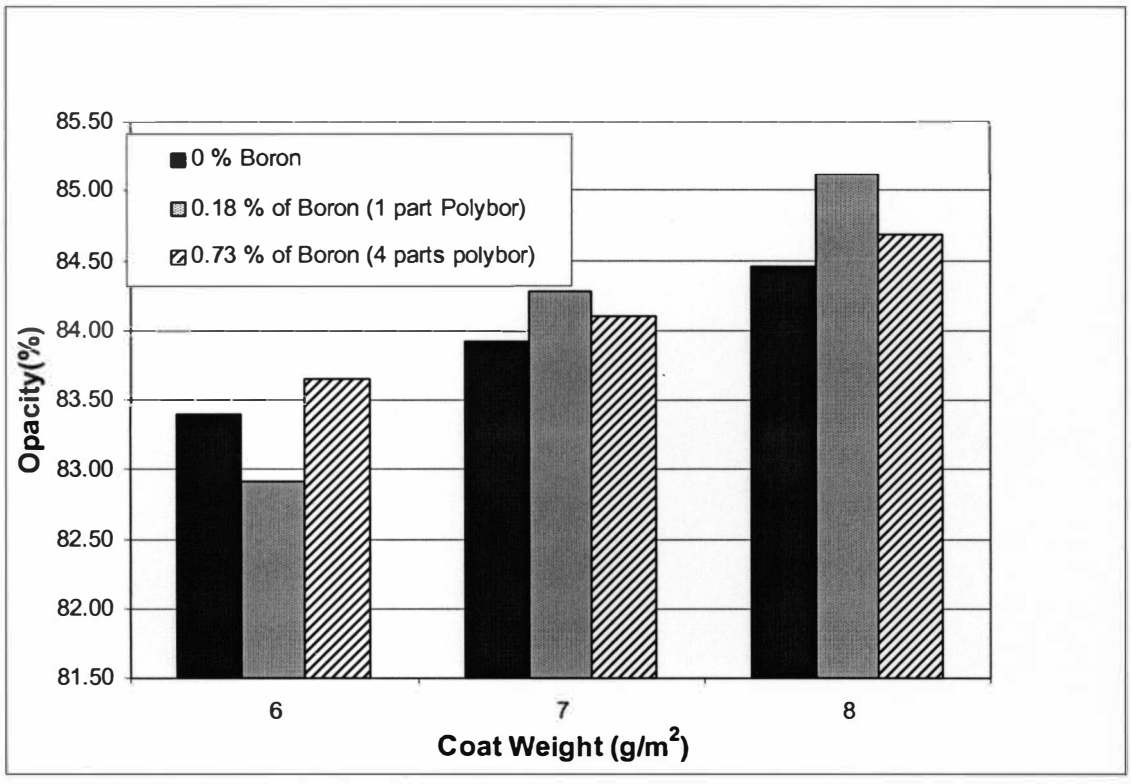

Figure 4: Effect of Polybor on Hydrocarb system

From Figure 4, it is observed that for Hydrocarb systems at low coat weights here is no effect of boron on the coating opacity. But, as the coat weight increases, there is a considerable increase in the opacity values up to 1.5%. It is interesting to observe the negative effect of boron at high coat weight. At higher coat weights, opacity is higher for coatings with 0.18 weight percent of boron, rather than for the coatings with 0.73 weight percent of boron.

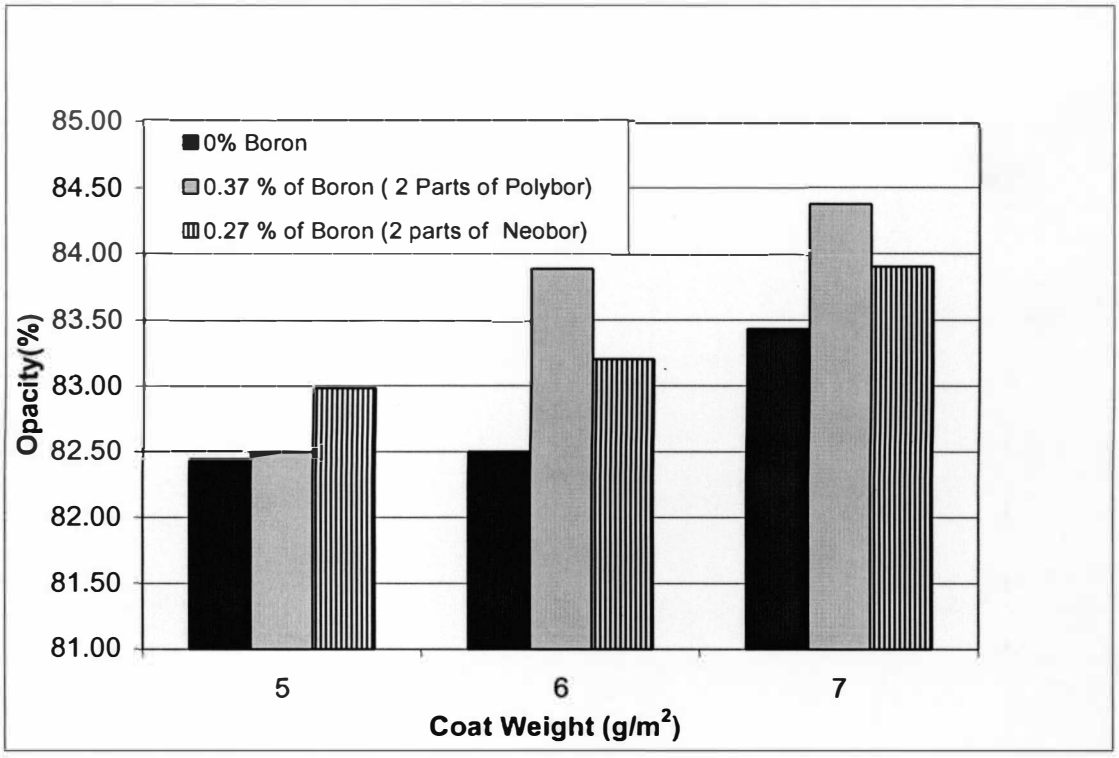

Figure 5: Comparison of borates with Hydrogloss system

From Figure 5, it is observed that for Hydrogloss systems as the coat weight increased there is a considerable increase in opacity. If considered in terms of Polybor and Neobor, Polybor has more effect on opacity than Neobor at the same coat weight. If considered in terms of percentage boron, as the percentage of boron increases, there is an increase of 1.5% in the coating opacity.

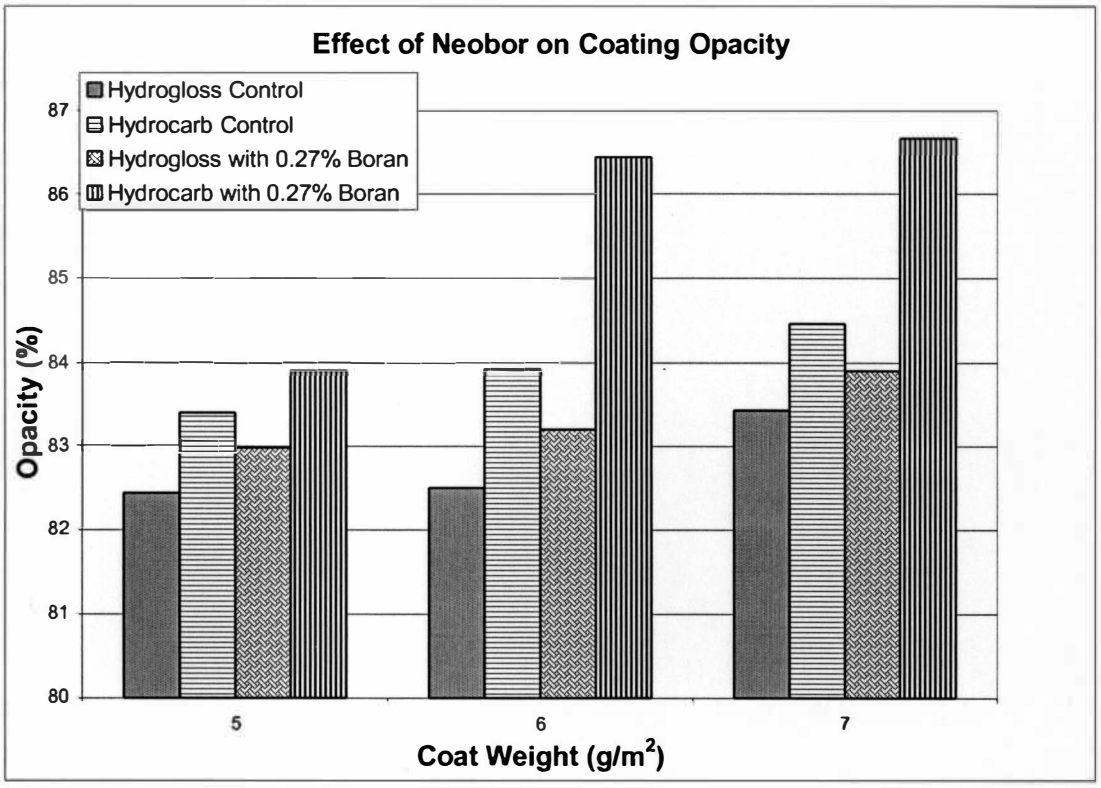

Figure 6: Effect of Neobor on coating opacity for different coating systems

In Figure 6, compares the effect of Neobor on both clay and carbonate systems. In comparison to the control coating, the opacity of the carbonate formulation is higher then the opacity of clay coatings at any given coat weight. Even for the systems with 0.27 weight percent boron, the coating opacity is higher with hydrocarb systems. If the boron coatings are compared with control for both Hydrocarb and Hydrogloss systems, there is a considerable increase in the opacity with the borate systems as the coat weight is increased.

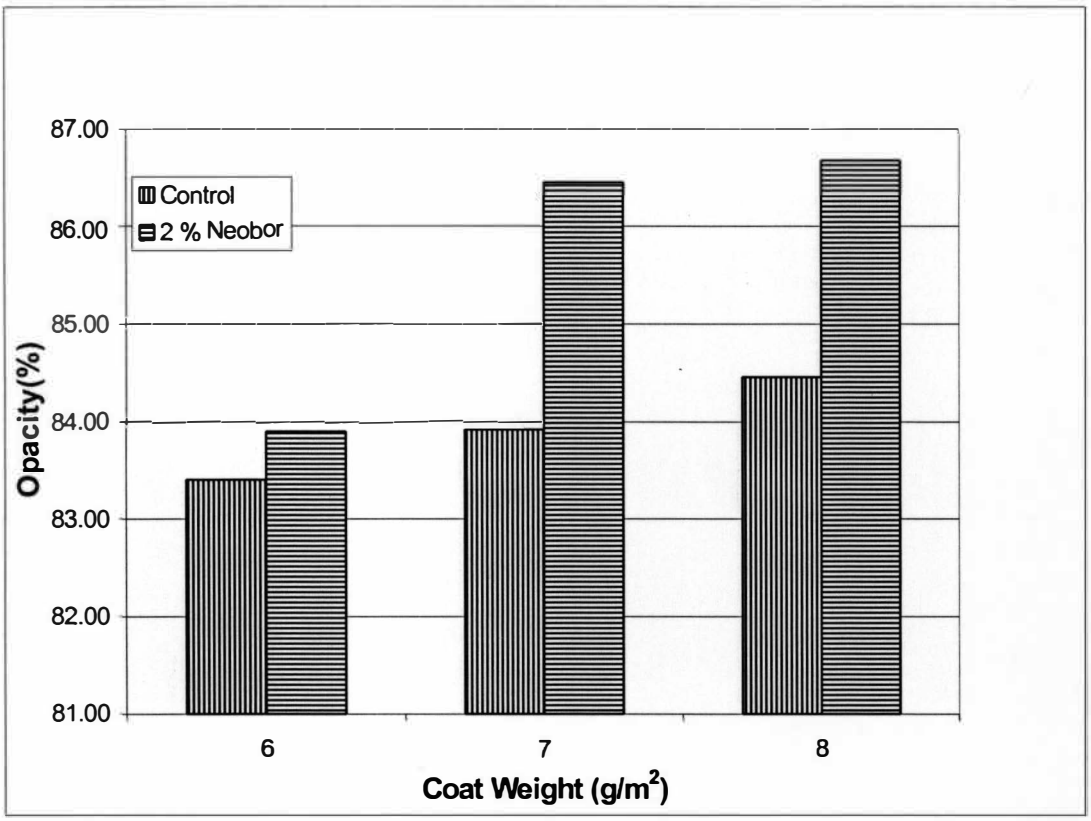

Figure 7: Effect of Neobor on coating opacity of Hydrocarb system

From Figure 7, it is clear that when compared with the control system, samples with 0.27 weight percent of boron have higher opacity. It is also observed that as the coat weight increases from 6 gsm to 8 gsm there is an increase of 3.3 % in the opacity.

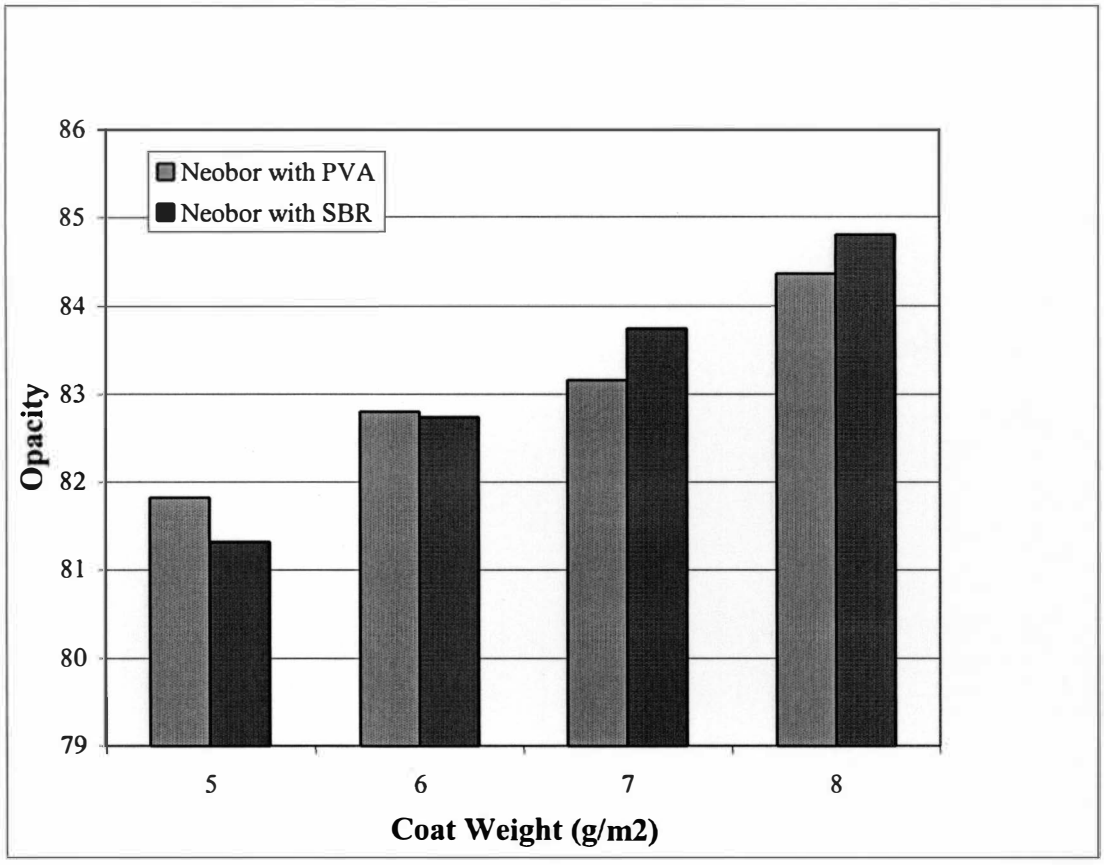

Figure 8: Effect of Neobor on SBR and PVA binder systems

From Figure 8, it is observed that Neobor has a positive effect both on SBR and PVAc binders. If the SBR and polyvinyl systems are compared, as the coat weight increases from 5 gsm to 8 gsm, there is more increase in the opacity of the SBR systems. Even in the PVAc systems, as the coat weight increases from 5 gsm to 8 gsm there is an increase of 3.9 percent in the opacity. In SBR systems, the increase is about 4.3 percent.

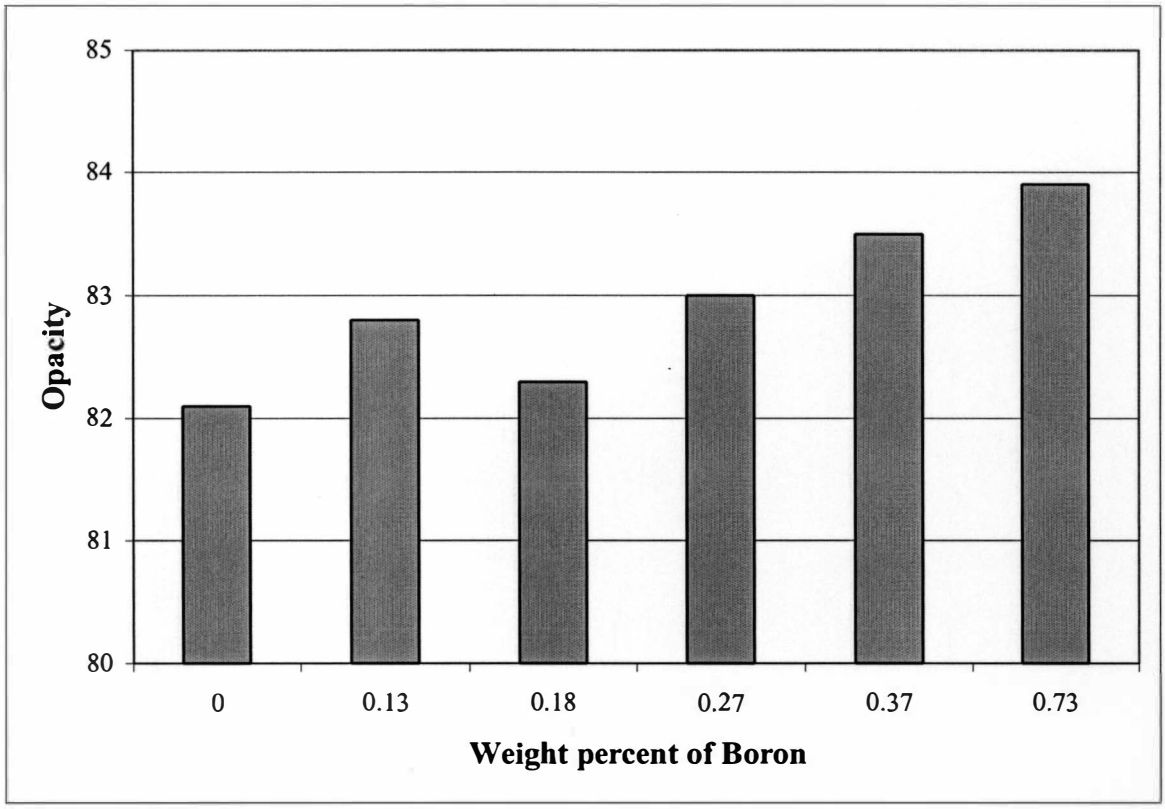

Figure 9: Opacity as a function of boron at different weight percentages

If coatings at the same coat weight (5gsm) with different weight percent of boron are considered, from Figure 9, there is a considerable increase in the value of opacity. If the control sample, i.e., having zero percent boron is compared to a sample containing 0.73 percent of boron, there is an increase of 2.2 percent in the opacity value.

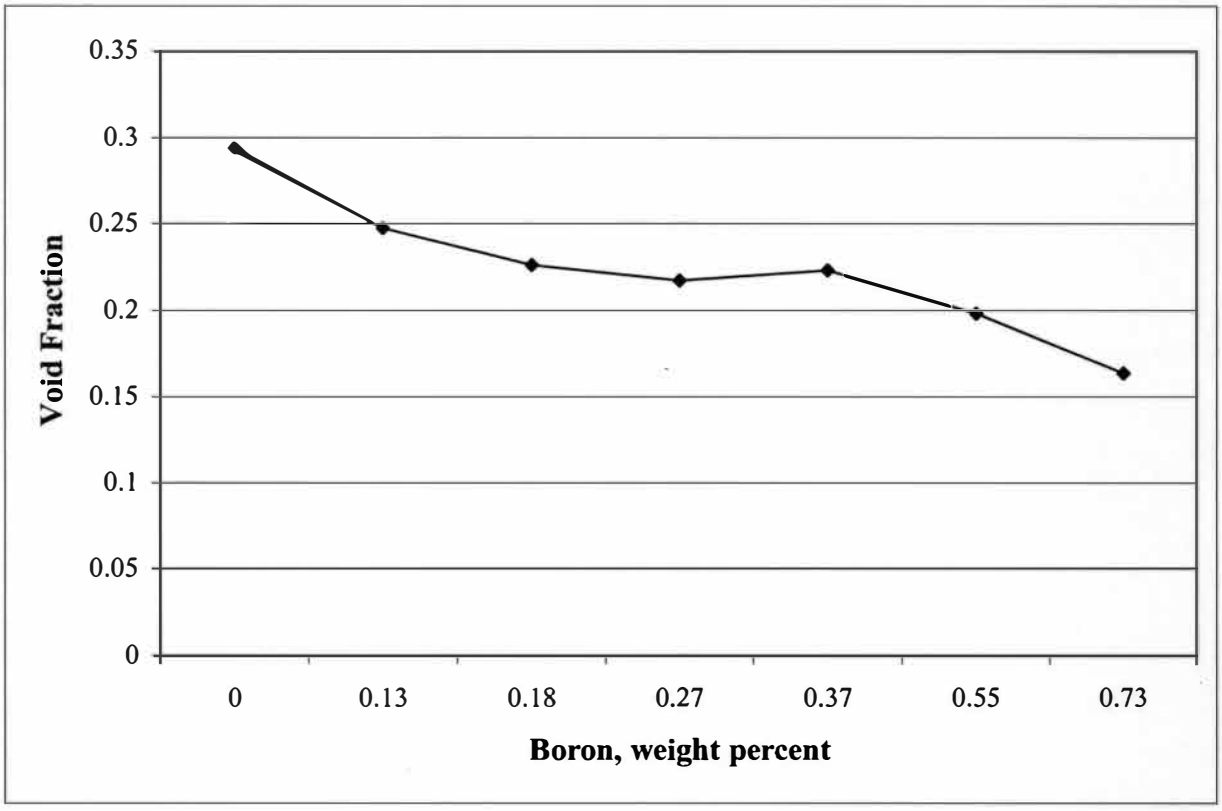

Figure 10: Void fraction as a function of boron at different weight percentages

Void fraction is the ratio of volume of air in the dry coating layer divided by the total volume of the coating. From Figure 10, it is clear that as the boron percentage increases, there is a decrease in void fraction. The decrease in void fraction is believed to contribute to the increase in opacity of the coated papers. Void fraction is a function of density, as density increases the void fraction decreases.

From fig 10, as the boron level is increasing there is decrease in void fraction values which indicates the less number of voids in dry coating. Since void fraction studies are done on Mylar sheet, there will be no penetration of pigments and water in to the sheet. All the solids are on the surface as there is no migration of coating components in to the surface. So the applied coating is denser on the surface, which explains the decrease in void fraction values.

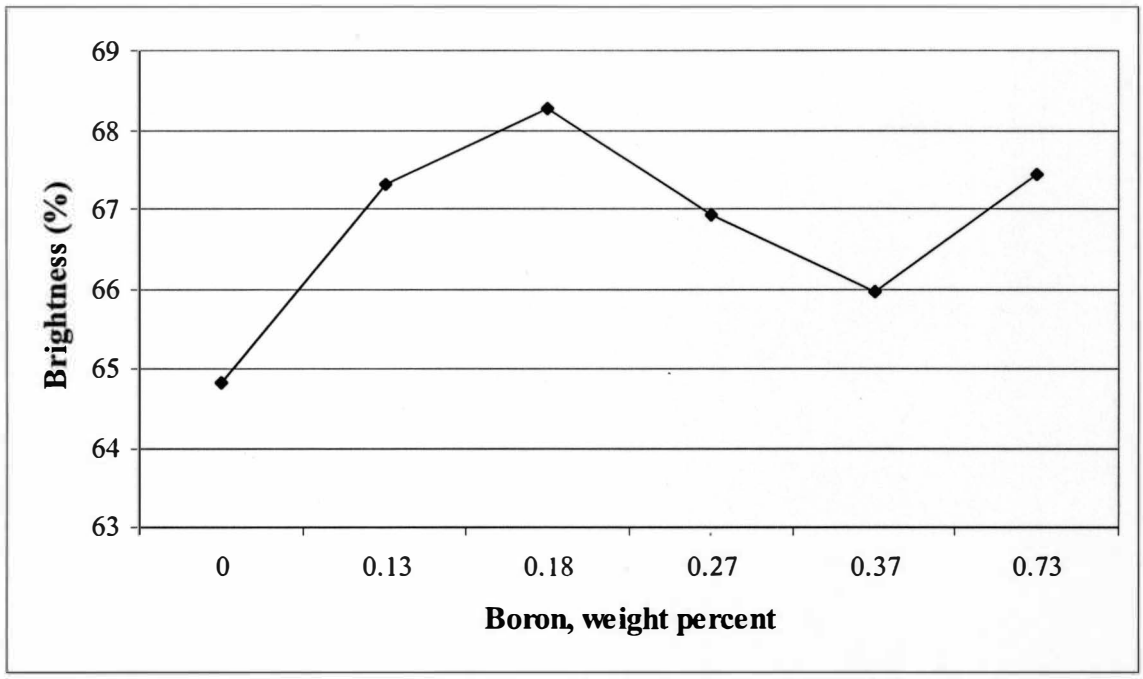

Figure 11: Brightness as a function of boron at different weight percentages

Figure 11, shows the brightness as a function of boron concentration. There is an increase of brightness with borate samples when compared with control samples without boron. Even though there is no particular trend in increase, Figure11 shows 5% increase with the addition of boron.

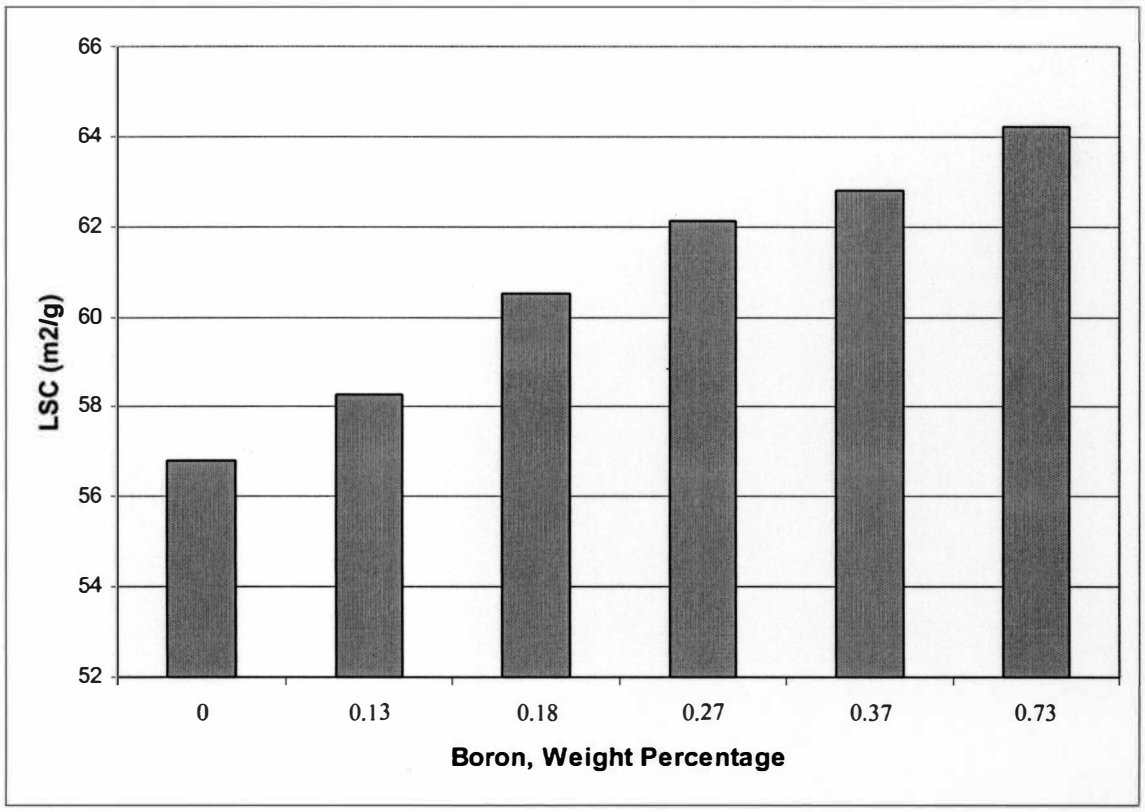

Figure 12: Light Scattering Coefficient as a function of boron

Figure 12, shows light scattering coefficient as a function of boron. The LSC was calculated by the reflectences at the wavelength of 457 nm, using Kubelka - Munk theory. The LSC value is increasing as boron level increases. This is supported by the increase in opacity values with boron level.

LSC values are dependent on the total reflectance from the coated sheet. The increase in reflectance may be due to additional medium in the coating formulations. The increase in LSC values may be due to the increase in number of voids on the surface. From void fraction values, it was observed reduction in of number of voids. Substrate being the different, migration of coating particles plays an important role.

Effect of borates as infrared drying agents

In Phase III, the infrared drying rates of the coatings were studied. From Phase II, it was observed that there is a considerable change in the opacity values for borate coatings when compared with the control, i.e., without borates. Both Neobor and Polybor have a positive effect on the opacity. Even though it was initially planned to study the drying performance of all six coatings, due to limitations in the experimental procedure, only one coating was selected for further study. So, studies were confined to only two coatings, one control and other with boron.

For this purpose, Hydrogloss with SBR was taken as the control system and to study the infrared drying, clay with 2 parts of Neobor was selected. For study, intensity and time are fixed on the laboratory infrared dryer.

Sample No.	% Change in Moisture	Initial Coat Weight, gms	Final Coat Weight, gms	Coat Weight, gm/m^2	% Change in Moisture per Unit Weight
1	5.37	1.2369	1.1704	17.96	.2989
2	5.67	1.2465	1.1758	18.48	.3068
3	4.32	1.2302	1.1770	18.60	.2322
4	5.74	1.2425	1.1711	18.03	.3183
5	4.59	1.2492	1.1918	20.05	.2289
6	4.84	1.2826	1.2206	22.89	.2114
7	5.75	1.2913	1.2191	22.74	.2528
8	4.70	1.2691	1.2095	21.80	.2155
9	5.92	1.2584	1.1839	19.30	.3067
10	5.83	1.2649	1.1911	20.01	.2913
11	5.50	1.2518	1.183	19.19	.2866
12	5.37	1.2388	1.1723	18.14	.2960
13	4.28	1.2017	1.1503	15.99	.2676

Table 7: Infrared drying results for Hydrogloss and SBR system

Sample No.	% Change in Moisture	Initial Coat Weight, gms	Final Coat Weight, gms	Coat Weight, gm/m^2	% Change in Moisture per Unit Weight
1	3.24	1.2456	1.2052	21.36	.1516
2	2.89	1.2006	1.1659	17.52	.1649
3	3.61	1.2694	1.2230	23.10	.1562
4	3.02	1.1986	1.1624	17.17	.1758
5	3.65	1.2384	1.1931	20.18	.1808
6	2.36	1.2019	1.1735	18.26	.1292
7	3.60	1.2674	1.2217	22.90	.1572
8	2.37	1.2437	1.2142	22.24	.1065
9	2.43	1.2585	1.2280	23.62	.1028
10	3.21	1.1926	1.1544	16.32	.1966
11	4.19	1.2720	1.2188	22.71	.1845
12	3.15	1.1915	1.1541	16.36	.1925
13	4.24	1.2461	1.1932	20.19	.2100

Table 8: Infrared drying results for Hydrogloss, SBR, and Neobor systems

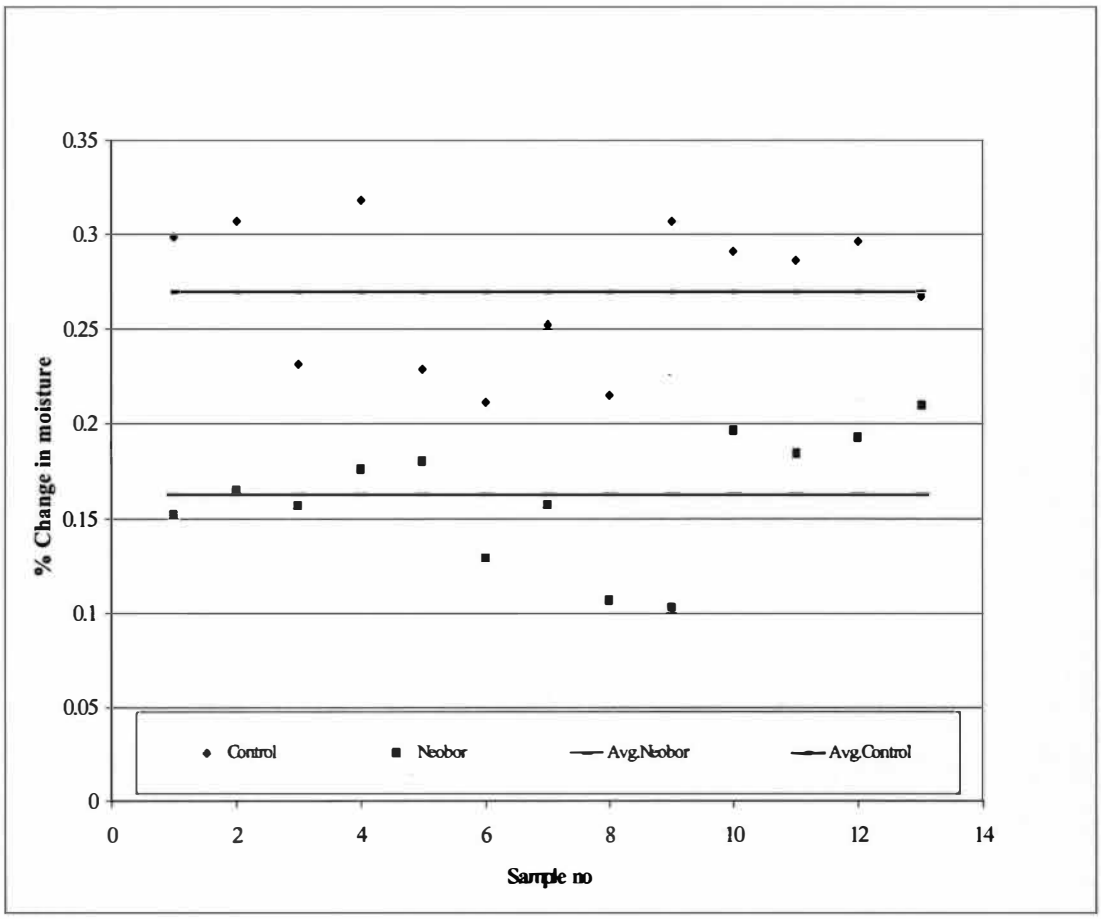

Figure 12. Effect of boron on infrared drying rates

Figure 12 shows the percent change in moisture in laboratory microwave for both the control samples and boron samples. From Tables 7 and 8, it is very clear that the change in moisture is less for boron containing samples when compared to samples without borate. This indicates that borate samples dried faster than the control samples. All the samples were dried under the same conditions (time and intensity), and the residual moisture measured. Using this method, it was determined that the boron samples dried more quickly, indicating the borates improved IR absorption efficiency of the coatings.

CHAPTER VI

ECONOMIC EVALUATION

Application of a drying system for coated paper grades on modern off machine or on machine coating lines typically include the use of IR, air floatation, and cylinders. The most common method of communicating drying is the use of drying rates, mostly stated in terms of pounds of water evaporated per unit width. In general 20-30% of the drying is done by infrared dryers followed by 60-70% by airflotation dryers.

In commercial applications containing top coat and base coat, energy costs are around 15% of the total production costs and coating chemicals cost around 30%. Here from the experimental results, it is observed that there is an increase of 2% in drying rates (From Table 7 and 8), if we compare the samples with same coat weight (apr.20.00g/m^2). On large production scale by replacing the expensive Titanium dioxide ($ 100.00/ 100 dry lbs) with cheap borate (app. $65.00/ 100 dry lbs) there is the possibility of reduction in the running cost with out affecting the optical properties as seen from the figures 9 and 11.

To estimate the economic suitability of the usage of borates in coating formulations, the following equations were used.[1]

The water load required for dryer section (EV) is,

EV = (CW/RM) *S *60 *(R1-R2)

Where,

EV = water evaporated for foot of width (lbs/hr)

CW = Coat weight (lbs)

RM = Ream size (sq. ft)

S = Speed (ft/min)

R1 = Ratio of water to solids entering the dryer

R2 = Ratio of water to solids exiting the dryer

Heat load on the dryer section (Q) is

$Q = (WT/RM) * S * 60 * SH * \Delta T$

Where,

Q = energy for foot of width (btu/hr-ft-width)

WT = Basis weight dry (lbs)

SH = specific heat of substance (btu /lb ^{0}F)

ΔT = temperature rise (^{0}F)

For calculation of energy requirements and drying rates of IR dryer, we will take

Basis weight (WT)	60lb/rm @ 4% moisture
Ream size (RM)	3300ft^2
Coat Weight (CW)	8 lbs
Coating Solids (CS)	60%
Speed (S)	2000ft/min
IR drying load (IR)	reduce coating from 60% to 70% dry.

Since the IR unit is located in the initial stages of the drying arrangement, the pre-heat phase, we will need to calculate the sensible heat load as well as the evaporation load.

The amount of water to be evaporated to reduce the coating solids from 60% to 70% with the IR dryer is

EV = (8/3300)* 2000* 60* (40/60-30/70)

= 69.2 lb/hr-ft-wd

EV load = 69.2 * 1000 btu/lb

= 69,200 btu/hr-ft-wd

Sensible heat load will be

Paper = [60-(60*{4/96})]/3300* 2000* 60* 0.35 * 100

= 73,181 btu/hr-ft-wd

Moisture = [60*{4/96}]/3300* 2000* 60* 1.0* 100

= 9,090 btu/hr-ft-wd

Coating = (8/3300)* 2000* 60* 0.5* 100

= 14,545 btu/hr-ft-wd

Water = [({8/0.6}-8)/3300]* 2000* 60* 1.0* 100

= 19,393 btu/lb-ft-wd

Total Q = Q (paper) + Q (moisture) + Q (coating) +Q (water) + EV load

= 185,469 btu/lb-ft-wd

As the drying rates are improved by 2% by the addition of borates, after the initial drying stage, the % of solids will be 70.2%. With this new % of solids

EV = (8/3300)* 2000* 60* (40/60-29.8/70.2)

= 70.4 btu/lb-ft-wd

Total Q = 186,657 btu/lb-ft-wd

So from the above it is observed that for the increase of 2% drying, IR dryer requires around 1,200 btu/lb-ft-wd. With the addition of 0.27% boron, the coating is reached to higher percent of solids with out any additional requirement of power. If

we consider in terms of production rate, for the above specifications the tonnage will be 14.5 tons/hr. For this production, IR drying capacity will be around 580lb/hr, but with the addition of borates it is increased to 595lb/hr. There is power savings of about 0.6% with the addition of 0.27% of boron.

Even though opacity values of borate coatings are not compared with TiO_2 formulations, there is a considerable increase in the opacity values when compared with control coatings. There is a possibility of replacing certain parts of TiO_2 with boron with out affecting the properties of the coated paper. This will further adds to the economics of the production.

CHAPTER VII

CONCLUSIONS

1) Borates interacted with both the Hydrocarb and Hydrogloss pigments.

2) Borates interacted with both SBR and PVAc binders.

3) The viscosity of the Neobor formulations was less than the other borates indicating it is less interactive with the binder and pigments than the Polybor.

4) The Polybor had the most positive effect on coating opacity.

5) The interactions between the borates and coating constituents increased with the concentration of boron used.

6) The opacity of the Hyrdocarb/borate coating was higher than the Hydrogloss/borate coating.

7) The borates influenced the opacity of the SBR coatings more than the PVA coatings.

8) The Neobor samples dried faster than the coatings containing no borate. A 2% increase was observed, indicating that the borates did have a positive effect on drying efficiency of the coating.

CHAPTER VIII

RECOMMENDATIONS

In this study only basic formulations were studied, to determine the effect on drying. But, the results showed its bulking capacity and improvement in opacity values.

In the laboratory, only up to 4 parts of borate was used based on the rheological data obtained from previous studies. Even though this study got positive results on borates as infrared drying agents, we are confined only to 2 parts of Neobor (only 0.27 weight percent of boron). The results showed 2% increase in drying rates with 0.27% of boron, there is a large scope for the improvement in drying rates if studies were done with higher percent of borates.

IR studies could not be performed on the CLC coater due to the inability to control coat weight. Higher coat weights were needed than could be applied by the CLC coater. So the samples were prepared by drawdown method, and due to limitations in the experimental procedure, we were limited to one intensity of radiation.

Even though initial studies with Polybor also observed improvement in drying rates, there is not enough data to compare the results. Here in this study, evaluation of borates as infrared drying agents was important so only basic coating formulation is considered. There is a need a to study the drying effects with different borate formulations on a mill trail, because with the laboratory trails we had limited information.

Here in this study only samples with, and without borates were compared, and borate samples showed improvement in opacity. Since borates are cheap replacements for expensive opacifing agents, its capacity as a bulking agents should be explored. There is a need of study with coating formulations replacing certain parts of Titanium dioxide with borates.

But at the same time, there is a need of study on borates, to check how borates are going to influence other surface properties. Other coating components, (lubricants, dispersants, OBA, etc.) not included in this study, because they may interfere or enhance the borate interactions within the coating systems. But with the study, borates are proved as increasing the drying rates, now there is a necessary to study borate interactions with all the coating components.

If we see in terms of end use, almost all papers are going through printing process. Print properties and runnability of printers is mainly based on surface properties of paper. So there is also need for running print trails for samples to check their printability.

APPENDIX

Equipment

Laboratory Infrared Dryer

For conducting IR drying studies, a laboratory IR dryer by Research Inc., was used. The high density infrared pyropanel is a modular, panel type heating unit that combines radiant and convection heating techniques. A forced airflow system turns waste heat into usable energy and allows the heater to operate efficiently at very high power levels. It uses tubular quartz lamps backed by a ceramic reflector to provide heat. For controlling the intensity and time of drying, a power controller (Model 5620 SCR Research, Inc.,) was used.

CLC 6000 (Cylindrical Laboratory Coater)

To check the runnability of the coating formulations, it was necessary to study the coatings at industrial conditions. Achieving the "right rheology" is crucial for a smooth coating operation and for optimal end properties of the coated sheet. In full-scale coating, and particularly when coating on-line, the properties of the coating color may change with time because of excessive dewatering, uncontrolled evaporation, or dilution. The changes in the coating color properties may be reflected in the behavior during application of the color and in the properties of the coated layer.

The CLC is a fast and reliable industry standard laboratory coater. The CLC 6000 provides an ideal means to test the coatings at industrial conditions.

Specifications and Capabilities of the CLC

Speed range: 300 - 6000 fpm (90 - 1830 m/min).

Base sheet capabilities: LWC to board, sheet size 20-40 inches wide by 11 feet long (51-102 cm wide by 3.4 m long). Rolls that are 39-40 inches (99-102 cm) wide and under 300 pounds (136 kg) in weight on a 3 inch (7.6 cm) core are preferred to provide enough for a comprehensive study.

Coater design: trailing blade or rod (grooved rods to simulate airknife coating), 5.5 inch (14 cm) coating width.

Coat weight control: uses a micrometer setting to move blade position in or out - wide coat weight ranges possible and wide ranges of coating solids can be run.

Drying: infrared, with controls programmable for pre-heat time and intensity.

Number of passes: double coating and coat-two-side possible.

OPACITY DATA

Sample No.	Coat Weight, g/m^2	Opacity of Control, %	Opacity of 1% Neobor, %	Opacity of 2% Neobor, %
1	5	82.44	82.76	82.98
2	6	82.5	82.94	83.32
3	7	83.43	83.2	83.9

Table A1. Opacity data for Hydrogloss and Neobor Systems

Sample No.	Coat Weight, g/m2	Opacity of Control, %	Opacity of 1% Polybor, %	Opacity of 2% Polybor, %	Opacity of 4% Polybor, %
1	5	82.44	82.14	82.5	81.32
2	6	82.5	83.14	83.88	82.15
3	7	83.43	83.64	84.37	83.74

Table A2. Opacity data for Hydrogloss with Polybor System

Sample No.	Coat weight, g/m2	Opacity of Control, %	Opacity of 1% Polybor, %	Opacity of 4% Polybor, %	Opacity of 2% Neobor, %
1	6	83.40	82.92	83.65	83.9
2	7	83.92	84.28	84.1	86.44
3	8	84.46	85.12	84.68	86.67

Table A3. Opacity data for Hydrocarb with Borate System

Sample no.	% of Boron	Brightness	Void Fraction	LSC
1	0	64.83	0.1656	56.8
2	0.13	67.3	0.1141	58.3
3	0.18	68.27	0.1272	60.5
4	0.27	66.93	0.1225	62.1
5	0.37	65.97	0.126	62.8
6	0.55		0.1286	
7	0.73	67.43	0.1174	64.2

Table A4. Brightness, Void fraction and LSC as a function of boron.

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