Improvement In Pigment Coating Performance With Synthetic Binders And Different Pigments

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ABSTRACT:-- The pigment coating performance is shown to have improved on using indigenous synthetic binders such as SB-latex and PVA in place of casein and pigments like alumina hydrate, modified talc products and fine ground calcium carbonate with kaolinite clay. Formulation prepared out of alumina hydrate with SB-latex and PVA imparts coating properties which are superior to that with titania. The techno-economical criteria of alumina hydrate being the future preferred coating pigment compared to titania, have been categorically explained.

The coating operation has been conducted in a laboratory air-knife coater and calendering in the mill. The ink density and show-through in printed strips, obtained from IGT printability tester have been quantified using new mathematical equations.

INTRODUCTION

Endeavour for improving the pigmented coating for enhancement of appearance and printability of paper continues to be of high technological interest all over the world (1). There is no clear definition of what pigmenting actually means (2). Normally it refers to a coating at the rate of 2 g/m² to 10 g/m² per side (2) but it can extend upto 17 g/m² (3) or more. Thicknesswise, it is of the order of ~8 -10 μ m (4). Coating converts the microscopic rough sites of the surface (4) suitable for superior printability properties compared to the uncoated paper. The roughness can be in micro or macro levels (5-7):

Micro roughness $-1 - 5 \mu m$

Macro roughness – $25 - 300 \ \mu m \ (50-100 \ \mu m \ of diameter)$.

The paper coating is a composite material consisting of pigment, binder and other additives along with air-filled voids (1). The void fraction of paper coating may range (1) from 20% to 40% depending

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on the pigment, binder and their addition levels. The void dimension (5) is 1-5 μ m. The coat applied on the paper or board masks the roughness and void spaces.

Paper coating binders are divided as (6): a) Water soluble colloids such as starch, protein, PVA and its derivates, b) Aqueous emulsion of synthetic styrene butadiene, PVA acetate and polyacrylate.

PVA is described (8) to be the strongest coating binder available from binding point of view (6). It is an excellent film former (6). It acts as an effective flocculant for the pigment suspension facilitating aggregation of particles (9). The PVA -Kaolin combination is described to be having Bringham plastic behaviour (9). PVA provides bridging of pigment particles. SB latex is rheology modifier (10) which brings pigment immobilization

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through an associative mechanism (10). In SB latex, styrene is the hard monomer and butadiene is the soft monomer that plasticizes the hard monomer; 50:50, 40:60 or 60:40 compositions of these two are normally used in paper coating.

Use of cobinders from styrene-butadiene (SB) latex and polyvinyl alcohol (PVA) from indigenous source has practically just commenced. The present paper will help building up confidence level in employing these synthetic binders which possess better coating efficiency than casein, commonly used in Indian mills now.

Alumina hydrate has already been established as an effective filler (11, 12) for manufacturing of quality paper barring aside the economic aspect. In case of use of alumina hydrate as coating pigment. the economic aspect can also be covered. Its use in paper and board coating is already practiced abroad (13). Somehow, it has yet to find use in paper manufacturing in India, specially with indigenous products. In order to make it more attractive in paper manufacturing, enhanced coating performance compared to the existing pigments, requires to be advocated. The present paper will show that alumina hydrate brings in enhancement in the coating performance, comparable to or better than that of titania. The present work is thus of quite economical importance.

The calcium carbonate and talc products used are also of new origins. As such calcium carbonate and talc are yet to find wide spread use as coating pigments in Indian paper mills. It is presumed that the comparative study made here will be of interest both to the pigment producers and paper mills.

Recently (14), we showed applications of empirical equations for quantitative evaluation of printability properties, determined in IGT printability tester with uncoated papers (1). It has been shown here that these equations are fairly valid for coated papers and boards also. Thus, the present results will serve quantification of ink density and show-through properties of coated boards which are evaluated only qualitatively in IGT printability tester presently (1).

The major development plans in big paper mills in India for obtaining enhanced coating performance are mostly aimed at procuring imported coating machinaries namely with higher speed, varying coat weight, premetering system replacing sizing press etc. The optimum machine performance for improving coating properties is unequivocally dependent upon the pigments and binders to be contained in the coating formulation. It may not be imperative to import the pigments and binders from abroad, thus necessiating search for indigenous improved pigment sources as well as production of binders.

In the present work, pigments of enhanced quality with modified properties and synthetic binders, all produced from indigenous sources have been employed. These results along with that from many sponsored projects undertaken in our laboratory, indicate plenty of scope to be existing for improving coating performance both from technological as well as economical points of view. It is felt that better coordination and participation of the mineral industries in the country can help for production of coating pigments with enhanced properties.

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EXPERIMENTAL

The base paper used here is of bamboo-hard wood pulp of 135 gms procured from the mill. The pigments and binders were all obtained from outside parties but from indigenous sources.

The coating experiment was conducted in the air knife coater with air pressure of 30-84 cm. of water. The coating formulations were prepared under controlled conditions using a mechanical stirrer with speed regulator. Water thermostat was used $(95^{\circ}C \pm 2^{\circ}C)$ for cooking of binders. Calendering of the dried coated papers was carried out in the mill. Printability tests have been carried out in an IGT printability tester and the optical properties in Elrepho brightness tester (15).

The following equations (1) have been used for quantitative determination of print density (PD) and show through (ST):

$$PD = \log \frac{R_{b}}{R_{p}}$$

$$ST = \frac{R_{p}}{R_{b}} X 100$$
(1)
(2)

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where Rb is the reflectance of the base paper determined using an opaque pad (10 sheets of base paper) and Rp is the reflectance after printing (measured with backing of 10 blotting papers). The reflectance values for print density have been determined from the printed side while show-through from the back side of the printed strip.

The ink used in IGT printability test is "IGT Reprotest B.V.-pick test oil for middle viscosity. The IGT pick resistance values are in cm. It represents the distance from which the picking starts. For oil absorption, PIRA surface oil absorption tester has been used.

"Show-through" is the property for which printed opacity test is carried out. In the present work the printed opacity has been determined by measuring the diffuse reflectance of back side of the printed sheet and the reflectance of an opaque pad of the unprinted side by Elrepho brightness tester and then taking their ratio. Though it is not very significant for coated paper, it has been observed that this property can very well be quantified and therefore, the results have been reported.

The print density has been determined from single value of ink layer. Print density (D) is expressed (16) by eqn:

$$D = Do (1 - e^{-cy})$$
 (3)

where D is print density of an infinitely thick ink layer and c is a constant. As the print density is nothing but ink film thickness at a particular, ink printing stage, it is quite logical to quantify print density with single IGT test. In fact, the method of determining 'D' in similar manner in all cases, allows correct comparison of coating performance with respect to various pigments and cobinders.

The particle size analysis has been carried out as per Tappi method (15). All other properties have been determined following to standard Tappi methods (15).

RESULTS AND DISCUSSION

SEM micrograph of the clay having layered structure, characteristic of phyllosilicate 1 : 1 or T-O-T (Tetrahedral silicate - Octahedral aluminate)

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group, is shown in Fig.-1 at 100 and in Fig.-2 at 1100 times of magnification. Talc belongs also to the mineral group of phyllosilicate possessing layering structure. Each sheet seen in the micrograph is constituted of infinite number of layers. Kaolinite clay has well defined platelets compared to talc. The stacking arrangement of plates and separation to individual platelets on shearing during preparation of coating colour are shown in Fig.-3. The gloss and other properties attributed to the coated sheet by kaolinite through its structural and textural properties are unique and therefore it occupies still the

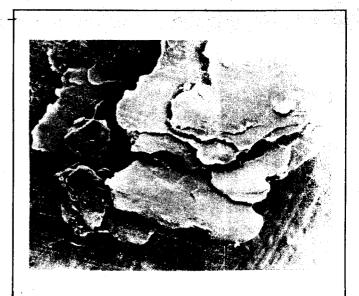


Fig.-1 : SEM micrograph of clay showing layering structure (X100)

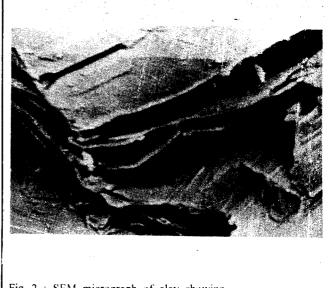
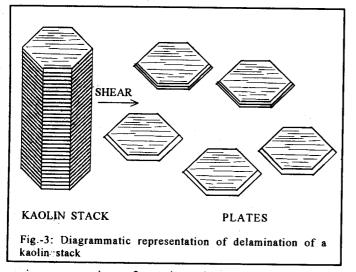


Fig.-2 : SEM micrograph of clay showing layering structure (X100)

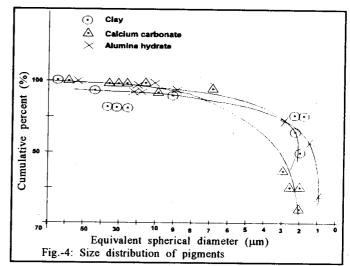


major proportion of coating pigment share all over the world.

Titania having higher refractive index (2.76 compared to 1.56 of clay) and brightness with finer particle size is used along with clay to supplement the deficiency in some of the properties of clay. The cost of titania is, however, becoming limiting factor for continuing use. Alumina hydrate having hexagonal platelet - like structure with high brightness and fine particle size, can be considered to replace titania. It has also excellent dispersibility property (15). Calcium carbonate is somehow being used more and more in Europe; out of 4.7 million tons, 48% is GCC and 48% is clay (17). Talc of better grade with brightness >93-94% is also available in the country now.

Coating grade alumina hydrate can be produced by varying the nucleation process in the precipitator during alumina refinary. Clay is beneficiated through steps of repeated washing, gravity separation, sedimentation, floatation and magnetic separation. The kaolinite coating clay available in India which is essentially in Kerala, cannot be processed to the extent as in abroad because of its natural mineralogical criteria. For exemple, in USA, coating clays (termed as ultrafine, bright or regular) have 93-98% particles finer than 2 μ m with brightness of 87-91% El. Such quality of coating clay is very difficult to get in India because of poor clay resources.

Therefore in order to meet coated product quality of international standard, our clay needs to be supplemented by other pigments with superior



textural and optical properties. Alumina hydrate appears to be the ideal supplementing pigment to clay.

The particle size distributions of different pigments are shown in Fig.-4. Kaolinite clay has 72% particles below 2 μ m; in calcium carbonate 52% is <2 μ m and 62% in alumina hydrate. However, percentage of particles below 5 μ m is ~85% in all the 3 pigments.

The brightness of titania is 96.2% El while it is 94.5% El in alumina hydrate. On the other hand, kaolinite clay has a brightness value of only 73.5% El.

The compositions taken with clay, titania and alumina hydrate are shown in Table-1 with formulation number I to IV; with talc in Table-2 with formulation number V to XI and with calcium carbonate from XII to XVII in Table-3.

Table-1

Compositions of formulations with clay, titania and alumina hydrate along with coat weight

Coating for mulation			Alumina hydrate,%		Cobinder	Coat weight (g/m ²)
I	100			SB Latex	PVA	15.2
П .	90	10		SB Latex	PVA	14.7
III			100	SB Latex	PVA	14.3
IV	90		10	SB Latex	PVA	15.0

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Table-2

Compositions of formulations with clay, and talc along with coat weight

Coating for- mulation no.	Clay (%)	Talc (%)	Binder Cobinder	Coat weight (g/m ²)
V	90	10 (A)	SB Latex PVA	14.3
VI	80	20 (A)	SB Latex PVA	14.9
VII	70	30 (A)	SB Latex PVA	14.7
VIII	60	40 (A)	SB Latex PVA	15.1
IX	60	40 (A)	Casein SB Latex	14.3
Х	60	40 (B)	Casein SB Latex	15.5
XI	60	40 (C)	Casein SB Latex	15.0

Table-3

Compositions of formulations with clay and calcium carbonate along with coat weight

Coating for- mulation no.		CaCO ₃ (%)	Binder	Cobinder	Coat weight (g/m ²)
XII	90	10 (PCC)	SB Latex	PVA	16.3
XIII	80	20 (PCC)	SB Latex	PVA	15.9
XIV	70	30 (PCC)	SB Latex	PVA	15.2
XV	90	10 (GCC)	SB Latex	PVA	15.0
XVI	90	10 (PCC)	Casein	SB Latex	16.0
XVII	80	20 (PCC)	Casein	SB Latex	16.5

Titania and alumina hydrate based coating formulations have been prepared with SB latex as binder and PVA as cobinder (Table-1) while for talc (Table-2) and calcium carbonate based formulations both SB latex-PVA and casein-SB latex binders have been taken. Apart from 100% clay and alumina hydrate, 10% replacement of the clay with titania as well as alumina hydrate have been made (Table-1).

3 types of talc have been employed; one is the common filler grade talc available already and the two others have been produced under special conditions with higher brightness. As both kaolinite and talc have lamellar structure replacement of kaolinite with talc should structurally make little difference and therefore replacement of kaolinite clay upto 40% has been made (Table-2). Precipitated calcium carbonate (PCC) and ground calcium carbonate (GCC) have been replace by 10-30% and 10-20% respectively (Table-3).

It can be seen in these tables that the coat weight has varied from 14.3 to 16.5 g/m^2 . The cal-

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cium carbonate based formulations in particular present higher coat weights $(15-16 \text{ g/m}^2)$ than the other pigments $(14-15 \text{ g/m}^2)$. Coat weight depends upon the pigment properties as the solid content in the formulations and air pressure in Air knife coater were kept constant.

Results in Table-4 for brightness confirm that the paper coated with 100% alumina hydrate has higher brightness value (78.9% El) than paper coated with 10% titania in china clay combinations (77.1% El). Out of the remaining systems, composite no. IV has 74.1% El where alumina hydrate is 10% with 90% of china clay. The coated product with casein and SB latex is found to have lower brightness than PVA-SB latex with same pigment combination (10% alumina hydrate and 90% clay). The highest opacity value (Table-4) is observed (97.54%) in composition IV which consists of 10% alumina hydrate and 90% china clay marginally higher than even that with 10% titania-90% china clay. The gloss values in Table-4 show that the best performance is with paper coated with 100% alumina hydrate (62%) and then in IV where the composition is 10% alumina hydrate and 90% china clay (59%). The titania based coated paper has 54% of gloss.

The brightness, opacity and gloss values of clay-talc pigment combination given in Table-5

Table-4

Optical properties of paper coated with clay, titania and alumina hydrate

Coating for- mulation no.	Gloss (%)	Brightness (%)	Opacity (%)
I	53	73.5	97.08
II	54	77.1	97.01
Ш	62	78.9	96.11
IV	59	74.3	97.54

Table-5

Optical properties of paper coated with clay and talc

Coating for- mulation no.	Gloss (%)	Brightness (%)	Opacity (%)
v	35	74.9	95.20
VI	40	74.9	94.49
VII	50	74.0	94.89
VIII	42	74.6	95.40
IX	34	73.2	95.45
х	29	72.0	95.57
XI	27	72.3	95.39

indicate that these values are lower than the clayalumina hydrate combination (Table-4). Gloss value of 50% has, however, been achieved where talc was replaced by 30%. It is again interesting to see that the gloss value increases from 35% at 10% addition of talc (V) to 50% at 30% of talc (VII). Thus, talc helps in increasing the gloss property of coated sheet. It is also important to note that the compositions IX to XI having casein-SB latex binders impart lower gloss values (27-34%) than SB latex-PVA binder systems. Use of PVA thus can be advocated for improving the gloss values of the coated boards. The brightness values of similarly boards coated with SB latex-PVA binders are higher than that with casein-SB latex by 2-3% El. However, the opacity values with both the binder systems remain same or rather casein-SB latex has marginally better values than with SB latex-PVA systems.

The optical properties of clay-calcium carbonate pigment combinations are given in Table-6 for compositions XII to XVIII. The GCC based coated sheet (XV) imparts higher gloss value than the PCC; 45% in former in stead of 32-39% in PCC. Unlike in case of talc, the gloss values are found to have

Table-6

Optical properties of paper coated with clay and calcium carbonate			
Coating for- mulation no.	Gloss (%)	Brightness (%)	Opacity (%)
XII	39	73.1	96.15
XIII	38	72.7	95.60
XIV	32	72.3	96.52
XV	45	70.9	95.87
XVI	32	72.7	95.84
XVII	37	72.5	96.23

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Oil absorbency and printability properties of paper coated with clay, titania and alumina hydrate

Coating for- mulation no.	Oil absorbency (Sec.)	Ink density (x 10 ⁻²)	Pick resistance (Cm.)
1	140	28.06	2.5
II	116	27.56	No pick
111	48	27.41	0.5
<u>IV</u>	135	28.77	No pick

decreased on increasing the pigment percentage: 39% at 10% PCC to 32% at 30% PCC addition. The brightness values have also decreased from 73.1% to 72.3% correspondingly but the opacity values have only marginally varied. The variation between the SB latex-PVA and casein-SB latex binder systems is found to have practically no effect on coated properties.

The oil absorbency values (Table-7) range from very low (48 sec.) in 100% alumina hydrate based coated product to 140 sec in 100% china clay. The coated sheet with 90% clay-10% titania and 90% clay-10% alumina hydrate both possess good oil absorbency values, 116 and 135 sec respectively indicating easy ink penetration to occur during printing.

The printability properties of the first four compositions presented in Table-6 indicate that the ink density value of IV (28.77 X 10^{-2}) containing 10%alumina hydrate and 90% china clay is higher than systems with titania (27.6 x 10^{-2}) and others. The coated sheets containing 100% clay (I) and 100% alumina hydrate (III) both have picks. However, the

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Table-8

Oil absorbency and printability properties of paper coated with clay and talc

Coating for- mulation no.	Oil absorbency (Sec.)	Ink density (x 10 ⁻²)	Pick resistance (Cm.)
V	150	27.73	No pick
VI	175	29.19	No pick
VII	220	28.54	No pick
VIII	225	27.99	No pick
IX	350	28.34	No pick
X	326	29.05	No pick
XI	310	28.07	No pick

Table-9

Oil absorbency and printability properties of paper coated with clay and calcium carbonate

Coating for- mulation no.	Oil absorbency - (Sec.)	Ink density (x 10 ⁻²)	Pick resistance (Cm.)
XII	225	29.56	No pick
XIII	165	27.53	No pick
XIV	66	27.96	No pick
XV	345	28.63	No pick
XVI	262	28.38	No pick
XVII	210	27.15	No pick

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 10°_{\circ} alumina hydrate containing coated sheet presents no pick similar to the 10% titania based coated sheet in Table-7.

Similar properties for talc-based coated sheets in Table-8 indicate that no picks are observed. The oil absorbency values are on the higher side which may cause more of ink penetration than that of titania and alumina hydrate based coated sheets. It is interesting to see however, that the ink density values are quite comparable or in some cases better than that in Table-7. Casein-SB latex systems have comparatively higher oil absorbency values than SB latex-PVA systems.

The coated sheets with calcium carbonate (Table-9) similarly show comparatively higher oil absorbency values than talc or alumina hydrate based coated papers. Here also, the ink density value of GCC is better than PCC containing coated products irrespective of the binder systems. The products are all free from picks in the printability tests.

The show-through value (96.1%) of papers coated with 100% china clay is best followed by (95.35%) system of 10% alumina hydrate and 90% china clay. The titania containing paper has 94.13% of show-through. According to Equation-2 higher the show-through values, better is the coating property.

The wax pick up values of various coated papers have been measured but not reported. The paper coated with 10% alumina hydrate and 90% china clay with PVA-SB latex cobinder has higher wax pick up value than the titania based product. The paper coated with 100% alumina hydrate (I) and 10% alumina hydrate - 90% china clay with casein-SB latex have wax pick up value of 4.

The printing gloss values are determined by placing the printed strips on a based paper and then examining in the gloss meter. The relative values for compositions I to IV are fairly higher than the others. The results of heat treated alumina hydrate will be presented in another publication.

CONCLUSIONS

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Alumina hydrate acts as an effective coating pigment with properties superior to that of titania on 10% replacement of kaolinite clay. Compared to

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titania, alumina hydrate improves the coated paper properties in gloss by 8%, brightness by 1.8% El with better printability properties. Opacity of titania based coated paper is, however, 97% while it is 96.1% with alumina hydrate. The new talc products appear to be quite promising, as gloss and other properties nearing to titania can be obtained. GCC has better coated paper properties than PCC. Talc can replace clay by 30 to 40% with improvement in coated properties. SB latex-PVA imparts superior coating performance of paper to casein-SB latex binders.

The results indicate that titania can be replaced by alumina hydrate with improvement in properties excepting opacity.

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