Study of Sodium Salt of Cashew Nut Shell Liquid (CNSL) as an Alternate Dispersant in Coating of Paper

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ABSTRACT

The principal reasons for applying a pigment coating to paper and paperboard are to improve printability and appearance. In its simplest form a pigment coating consists of a pigment and a binder that is present to bind the pigment particles both to one another and to the base sheet of paper. Pigments are the main constituents of pigment coating. It is very important that the pigment should be fully dispersed to ensure satisfactory performance and full contribution to the properties of the coated paper. A number of systems are used for pigment dispersion, all of which involve the addition of chemical dispersant and the use of mixing equipment that provides a sufficient amount of energy input to breakdown any particle clusters present in dry pigments. The chemical dispersant serves to aid in the wetting (displacement of gas) from the pigment particles, adjust the surface charges of the pigment particle to prevent flocculation, and reduce the viscosity. In this study sodium salt of CNSL was studied as a dispersant for china clay and calcium carbonate pigments. To study the dispersant a demand curve was plotted between Brookfield viscosity and dosages of dispersant. Sodium salt of sulfonated CNSL was found to be an effective dispersant as it decreased the viscosity of the pigment slurry to the minimum value of 200 cP at the optimum dose of 0.8%. A comparative study was done with a standard dispersant (poly acrylate) commonly used in paper mills. Finally the properties of the coated papers were studied. By socio economic concern and ISO 14001 (3R) Reduce, Recycle, Reuse the waste generated, from industries, is to be converted into valuable products. On the above concept CNSL, a byproduct of cashew industry is converted into a surfactant that finds valuable applications in pulp and paper industry as slimicide, penetrating aid in pulping, insecticide, and additive in neutral rosin sizing and now as a dispersant in pigment coating.

Key words: *Sulfonated CNSL (SCNSL), Coating, Pigments, Dispersant, and Surface active agent.*

Introduction

There are many kinds of coated paper made in the world today. But pigment coated paper for printing is by far the most common to provide the printer with a sheet of superior surface for printing. It provides enhanced smoothness, better ink receptivity, higher whiteness, better printability and better gloss. The field of paper coating has grown in leaps and bounds over the last few decades simply because of the growth in demand for quality products that could withstand the printing operation.

The original pigment for coated paper, to improve printing, was clay and its dominance has not changed yet. Coating clay is a natural mineral, which is processed into many grades. They vary in brightness and whiteness, particle size and shape, dispersing and flow properties, affinity for adhesives, and their propensity to produce a shiny or dull coating[1].

Some commonly used pigments in paper coating include: kaolin clay or china clay, calcium carbonate, titanium dioxide, calcined clay, aluminium trihydrate, amorphous silica and silicates, satin white, talc, zinc oxide, barium sulfate and plastic pigments.

Traditionally clay is the major pigment used for coating on paper surfaces. The use of $CaCO_3$, both ground (GCC) and precipitated (PCC)[2], is increasing for technological reasons.[3,4] The other pigments like talc, titanium dioxide and synthetic (plastic) pigments are used relatively in smaller quantities.[5] More than one pigment is combined in coating formulations to achieve the desired quality.[6] Clay and other pigments are all dispersed in water, and many of their properties depend on their behavior in this state. The mineral pigments are stabilized by a dispersing agent[7] to prevent pigment particle flocculation, and under shear to prevent aggregation, which otherwise would result in sedimentation and high viscosity.[8] The dispersing agent is most often a highly charged synthetic polymer with relatively low molecular mass and sodium polyacrylate is often used.[9] In absence of dispersant, the pigment slurry can only be prepared at very low solid content. To obtain maximum benefit from any pigment, every particle must be wetted and clusters of particles separated. The large aggregates make the coating rough, they cannot be bonded properly to the base stock and in extreme cases they will break down under super calendaring and cause dusting. For proper coating color preparation,[10] pigments must be dispersed at the required solids content to minimum viscosity.

There are number of chemicals which cause the particles to wet and separate and at the same time lower the viscosity of the

slurry. The chemicals used as dispersants are anionic polymer dispersants, poly phosphates, alkali silicates, alkalis and nonionic polymer dispersants.

Anionic polymers have become the dominant dispersion chemical with the polyacrylics representing most of the volume. Other materials such as lingnosulfonate or naphthalene sulfonates are used to a limited extent. The alkali silicates rank second in use for coating pigment. Silicates are used quite a lot with primary clay and with secondary clays in the mining and processing industries. There are number of polyphosphates which can be used but, their shorter term stability and the desire to eliminate them from effluent[11] streams has sharply curtailed their use. Alkalis such as metal hydroxides are not considered real dispersants, but they can reduce the viscosity of a suspension by increasing the pH. They are sometimes used in conjugation with other dispersants.

Nonionic polymers and surfactants are used in special cases. The most common of these products are condensation products of fatty alcohols and ethylene-oxide. They are believed to have molecules that are two ended. One end is hydrophobic and the other is hydrophilic. The more hydrophobic end attaches to a pigment particle, while the hydrophilic extremely at the end of a polyethylene chain sticks out in the fluid and keeps the pigment particles apart.[12]

Sodium salt of CNSL belongs to the category of nonionic polymer dispersants. During the synthesis of this compound if slight excess of conc. H_2SO_4 is added, the molecule undergoes controlled polymerization (if excess of conc. H_2SO_4 is used, uncontrolled polymeration leads to a hard rubbery mass) and this gives rise to good dispersant property to the molecule. In the present study sodium salt of sulfonated CNSL was synthesized[13] by using slight excess of H_2SO_4 at 0-5 ^oC to get polymerized compound. It was then washed with water and then treated with 10% NaOH solution to get the sodium salt with pH = 9-10. A highly viscous, light brown color emulsion was obtained. The compound was studied for its dispersant properties in pigment coating of paper. The pigments used were clay and $CaCO_3$.

Experimental

Preparation of pigment slurry

Table 1 Preparation of pigment slurry

Contents	Amount
Water	215 ml.
NaOH	0.25 g.
Dispersant	0.2 – 1.6 %
Clay	400 g
$CaCO_3$	100 g
Total Solids	68-68.5 %

In the present work, to study the effect of sodium salt of sulfonated CNSL as a dispersant, clay and GCC were used as pigments. Clay and GCC were available as dry powders. Pigment slurries were prepared according to SCAN 55:85 method (as per Scandinavian pulp and paper testing committee procedure). For 400 g pigment (dry basis) the total solid content was targeted at around 70%. The pH of the slurries was adjusted to 7.5 to 8.0 by adding NaOH. Pigment slurries were prepared according to formulation in table 1.

Preparation of coating color

The pigment slurries prepared by using different doses of dispersants were converted in to coating colors by adding measured quantities of binder and other additives in the following sequence: CMC, lubricant, plastic pigment, NH_3, OBA and insolubiliser. The total solid content of the coating colors was targeted to 58-59% solids. The pH of the color was adjusted to 9.0 - 9.5 by adding ammonia solution. All coating colours were based on 100 parts per hundred (pph) pigment. Coating colors were prepared according to formulation in table 2.

Table 2 Composition of the additives used in coating color

Chemicals	Additives	Solids/solution (%)	Parts per 100 Parts of Pigment
Styrene butadiene	Binder	50	12
Carboxymethyl cellulose	Co binder	5	5
Calcium stearate	Lubricant	50	1.2
Polystyrene	Plastic pigment	50	1.2
Ammonia	Flow modifier	As such	1.0
2-2/ stilbene 4-4/ sulfonic acid	OBA	As such	0.2
Hydroxylated resin	Insolubiliser	25	0.35

Application of coating

The coating color was applied to the top side of a 300 g/m^2 base paper by using laboratory bar coater. The coated sheets were air dried in the laboratory. Some important properties of the base paper and coated papers were studied according to standard TAPPI methods

Evaluation of coated sheets

The coated sheets were uncalendard and tested for important sheet properties, results are tabulated in table 5 and 6. Following sheet properties were tested in the laboratory.

Brightness:

The standard brightness instrument has 45^{0}illumination and O^o viewing. The measurement is through a 457 nm filter and is based on the reflectance of magnesium oxide as being 100%. Test method TAPPI T 452 was used for brightness test.

Gloss:

It is specular reflectance of light, which is reflected at an equal and opposite angle. Normally measured at 75^o or 20^o high gloss surface is measured at 20^o, TAPPI methods T 424 and T 480 is used for gloss tests.

PPS (Parker Print Surf):

PPS leak instrument used extensively is calibrated in micrometers, which represents the average dimension of the gap between the paper and the metering land. TAPPI test UM 518 is used for measuring PPS.

Coat weight:

The determination of the weight of pigment coating applied to the paper is measured as coat weight by standard routine method in g/m^2

Pick strength:

Pick strength determines the resistance of the coating to being picked or pulled off the raw stock during printing. A wax pick test (Dennison wax) was used to test this surface property. Adhesive number, no Pick value sticks ranging from 5A, 6A, 7A, 8A were used. TAPPI test UM 463 was used for measuring pick strength.

Results

I Study of dispersant properties of SCNSL by replacing poly acrylate in pigment slurry

Pigment slurries were prepared by using both poly acrylate & SCNSL according to formulation in table 3. Brookfield viscosities were measured for pigment slurries prepared and recorded in table 3. Pigment slurry containing 0.8% poly acrylate was treated as standard (sample 1).

Table 3 Viscosity of clay slurries (using both poly acrylate and sulfonated CNSL)

Sample	Amount (%)		Brookfield viscosity (cP)
	polyacrylate	SCNSL	
1 (std)	0.8	0	550
2	0.6	0.2	540
3	0.4	0.4	515
4	0.2	0.6	470
5	0	0.8	200

II Dose fixing of SCNSL as dispersant

SCNSL was used from 0.4% to 1.6% (2.0 g to 8.0 g) in the preparation of slurries of clay. Viscosity of the pigment slurries were measured by using Brookfield viscometer Model LV DV - II, using 63 no spindle at 100 rpm. Table 4 shows the variation of viscosity with respect to sulfonated CNSL dose. For each dose three sets of readings were taken and mean of viscosity values were calculated. Properties of coated paper sheets were studied and are listed in table no 5

Discussion

- It is clear from table 3 that as amount of SCNSL increases 0.4 to 0.8 %, the viscosity of pigment slurry decreases. The decrease in viscosity is proportional to the % of SCNSL added in the pigment slurry. Looking in to these results it was decided to totally replace polyacrylate by SCNSL as a dispersant.
- In table 4 it is observed that viscosity decreases by increasing the dose of SCNSL from 0.4% to 0.8% and then increases on further increasing the dose above 0.8%. Thus 0.8% dose was considered as optimum dose for SCNSL as a dispersant.
- SCNSL as a dispersant gave better results than polyacrylate (table 4) which is commonly used as dispersant in clay coating.
- It is clear from table 5 that Replacement of polyacrylate by SCNSL has not much affected the coated sheet properties as the brightness of the sheets was 78.7 to 79.7, PPS was 4.5 to 5.3, coat weight was 9.16 to 13.36 and gloss ranged from 26.0 to 28.5.
- Brightness and gloss in table 5 for sample 1(standard) and 5 were found to be almost same. PPS of sample 5 was less than sample 1. Coat weight of sample 5 was more than sample 1.
- Sheet coated with coating color containing optimum dose of SCNSL (sample 10) was found to have comparable sheet properties with that of sheet coated with coating color containing same dose of polyacrylate (sample 1).
- In sample 13 and 14 lubricant was not used in order to study the role of sodium salt of CNSL as a lubricant. Sheets coated with these coating colors gave good

Table 4 Effect of SCNSL dose on viscosity

Sample	Amt of SCNSL (%)	Brook Field viscosity (cP)
6	0.4	325
7	0.5	306
8	0.6	275
9	0.7	240
10	0.8	200
11	0.9	210
12	1.0	260
13	1.2	340
14	1.6	365

Table 5. Properties of uncalendard coated papers

Paper sample	Properties				
	Brightness (%)	PPS (micron)	Gloss (%)	Coat weight (g/m^2)	Wax pick (no pick)
Uncoated	72.6	5.5	11.5	-	6A
Standard	79.7	4.8	28.5	11.6	7A
2	78.7	4.6	26.0	9.9	7A
3	78.7	5.3	28.0	9.2	7A
4	79.3	4.9	27.0	11.1	7A
5	79.6	4.5	28.0	13.4	7A
6	78.8	5.0	27.0	10.9	7A
8	78.9	5.1	28.0	10.0	7A
10	79.6	4.5	28.0	13.4	7A
12	79.6	4.5	27.0	13.5	7A
13	79.0	4.9	27.5	10.0	7A
14	79.2	4.9	26.0	9.7	7A

values of brightness and gloss. This shows that compound can also be used as lubricant.

- The viscosities of the coating colors were measured after a week of its preparation and the change in viscosity was found to be negligible unlike polyphosphates. This confirms that SCNSL provides long term stability to the coating color and is well suited for $CaCO_3$ dispersion as it is sensitive to time and temperature.
- Sulfonated CNSL is a complex mixture of sulfonated cardanol & cardol. The compound has SO_3H group on its benzene ring along with OH group and a long alkyl side chain $C_{15}H_{31-n}$. The physicochemical properties[14] show that it is a nonionic surfactant. The $C_{15}H_{31-n}$ chain part is hydrophobic and the other part is hydrophilic in nature. The hydrophobic end attaches to a pigment particle, while the hydrophilic portion sticks out in the fluid and keeps the pigment particle apart. SCNSL is surface active agent and is thus useful in helping to wet out the pigment. The basic objective of dispersion process is to intermix the fluid phase and the pigment to the point where each pigment particles is a separate entity individually surrounded by the fluid in a stable atmosphere that will not flocculate or settle. For paper coating an additional objective is to accomplish this at maximum pigment volume concentration (that is, at minimum fluid or void volume) to obtain a desirable rheology of the coating mixture, low binder demand, and good particle orientation in the final pigment coated surface.[15]

Conclusion

Sodium salt of sulfonated CNSL in pigment slurry decreases the coating color viscosity, at optimum dose of 0.8%. Coated paper sheets have shown increase in brightness, gloss and coat weight and decrease in PPS. Sulfonated CNSL has antimicrobial properties, thus it can provide long term stability for pigment slurry containing clay and $CaCO_3$. This study had also shown that sodium salt of sulfonated CNSL can be used as a lubricant in coating of paper. Above all, this compound is obtained from natural resources and its use is eco-friendly. The dispersant property of sodium salt of sulfonated CNSL can be extended to the other industries which mainly make use of clay as raw material for example paint and ceramic industries.

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Reference

1. Murray HH (1976). TAPPI Monograph series 38, Chap- 5.
2. Hagemeyer RW (1976). TAPPI Monograph Series 38, Chap-4.
3. Lehtinen E (2000). Pigment coating and surface sizing of paper, in Papermaking Science and Technology. Book-11, Fapet, Finland.
4. Duncan PA, Patrik KL (1995). PCC in coating formulas expected to rise dramatically this decade [1990-2000]. Pulp and Paper, 69(5), 141.
5. Malla PB, (2005). Advances in coating pigment technology, TAPPI Coating Conference and Exhibit, Toronto ON, Canada, Apr 17-20, 337.
6. Iyer RR (2005). Shapes and size engineering of kaolin pigments for improved coated paper performance. TAPPI Coating Conference and Exhibit, Toronto, ON, Canada, Apr. 17-20, 339.
7. Rohmann ME (1974). The influence of sodium polyacrylate on the properties of coating colors. TAPPI J. 57 (5), 96-100.
8. Sanders ND, Bashey AR (1991). Strength and interactions between papermaking polymers and particles: Wet end control and paper microstructure, International Paper Physics Conference. TAPPI Proceedings 473-482.
9. Snyder K L (1995). Dispersants in Paper Coating Additives, Chapter 6. Kane, R.J. Ed. TAPPI Press, Atlanta 1995 ISBN 0-89852-061-4/95.
10. Husband JC, Adams JM (1992). Interactions in clay-based rotogravure coating colors, In proc. Paper and Coating Chemistry Symposium 1992, Stockholm (Sweden), 2-4 Jun 1992 Nordic Pulp and Paper Research Journal (Sweden) v. 8(1) 216, 195-199.
11. Michaels AS (1958). Deflocculation of kaolinite by alkali polyphosphates. Industrial and Engineering Chemistry 50, 951-958.
12. Pulp & Paper Manufacture Third edition, TAPPI Press, Vol-8 Chap-I, 1-73.
13. Sharma S, Nair A, Pai KV (2010). Development of surface acting agents using naturally occurring phenols from CNSL by sulfonation, IJAC journal, 6 (2), 279-286.
14. Sharma S, Nair A, Pai KV, (2011): Study of antimicrobial properties of sodium salt of sulfonated cashew nut shell liquid (CNSL) for slime control in paper mill, IPPTA Journal, 23(2), 193-196.
15. Casey JP (1960). Pulp and Paper Chemistry and Chemical Technology, Third edition, volume VI, Pigment Coating, Inter Science Publishers, Inc, New York.