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Synthesising and Optimizing Of Thermochromic Inks

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Abstract

A method of making the solvent based ink formulation which includes a thermochromic pigment made from liquid slurry. Some pigment particles which either depict reversible or irreversible colouring material which exhibits a visible change in colour between a first colour state and second colour state in response to a change in temperature. Final selection of formulation and the chemistry behind its change has been the key factors. Temperature range for a normal beer bottle is considered as basis for the entire work.

Keywords: Thermochromic

INTRODUCTION:

Thermo-chromic flexographic inks, in printed form, are coloured below a specific temperature, and change to colourless or to another lighter colour as they are heated through a defined temperature range. These inks are available in various colours and activation temperatures [1]. These inks typically comprise an electron-donating substance, an electron-accepting substance, and a solvent which undergo a reversible colour change in response to change in ambient temperature, for example, from

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ambient to freezing or from ambient to elevated temperature. The colour change which takes place may be a change from one colour to another, from coloured to colourless, or from colourless to coloured.

Standard activation temperatures are 15, 25 and 43°C. Other activation temperatures are also available, from -5°C to 60°C [2]. The activation temperature is defined as the temperature above which the ink has completely changed to its opaque white, translucent or light color end point. The colour starts to fade at approximately 4°C below the activation temperature and will be in between colours within the activation temperature range. The color change is “reversible,” i.e., the original color will be restored upon heating. Flexographic ink is ideal for document security, promotional items, temperature indicating labels, packaging, games, novelties, etc. Thermo-Chromic pigments come in two forms, liquid crystals and leuco dyes. Leuco dyes are easier to work with and allow for a greater range of applications. These applications include: Battery testers, clothing, and the indicator on bottles of maple syrup and beverages cans, changing from white to blue to indicate the can is cold.

Leuco dyes allow wide range of colors to be used, but their response temperatures are more difficult to set. Under normal conditions, thermochromic leuco dye inks have a shelf life of 6 months or more. After they are printed, they function, or continue to change color, for years. The post-print functionality can, however, be adversely affected by UV light, temperature in excess of 121°Celsius and aggressive solvents [3]. Leuco dyes are microencapsulated into tiny droplets that are only about 3 to 5 microns in size, which prevents them from reacting with or being damaged by other chemicals. Usually, leuco dyes are coloured when they're at a cool temperature. Then, as heat rises, they become translucent, which lets them reveal any colours, patterns or words that may be printed on an underlying layer of ink. Leuco dyes can be blended with another colour so that as temperatures change, a two-tone effect occurs. Mix blue with yellow, for example, and you have an ink that looks green at lower temperatures and yellow when heat rises. The teensy capsules contain a colorant, an organic acid and a solvent. At lower temperatures, the solvent remains in a solid state, keeping the colorant and acid in close proximity to each other -- and as a result, they reflect light and create colour. As the solvent gets warm, the colorant and the acid separate and there's no visible colour, which in turn exposes underlying inks. When it comes to temperature accuracy, leuco dyes are more ham-handed than Thermochromic Liquid Crystals, so you can't depend on them for applications where you really need a precise temperature reading.

THERMOCHROMIC INK FROM LEUCO DYES.

Thermochromic inks or dyes are temperature sensitive compounds that temporarily change color with exposure to heat. They have various applications one of them being Leuco dyes. They are made from copper phthalocyanine (CPC) pigment which is one of the major components for the manufacturing of dyes and paints. The molecular structure of CPC is the key contributor to its colouristic properties, particle shape, size and crystal structure which play a decisive role in determining the final shade of the pigment[4].

Table 1.

Typical Properties of thermo-chromic inks

PROPERTIES	VALUES
Viscosity (Zahn 2)	35-55 Pa.sec
pH (initial)	7.3-7.4
Density (Approx.)	1.02 kg./ltr
Appearance Liquid	Depending on colour
Percent Solids (Approx.)	37% +/-
Solvents(Approx.)	<5% +/-

(Source:www.colourchange.com/updates last accessed on 19th Aug, 2017)

The use of copper phthalocyanine crude is done for manufacturing thermochromic inks. The following flow sheet shows the production of the crude.

PRODUCTION OF COPPER PHTHALOCYANINE THERMO-CHROMIC BLUE CRUDE:-

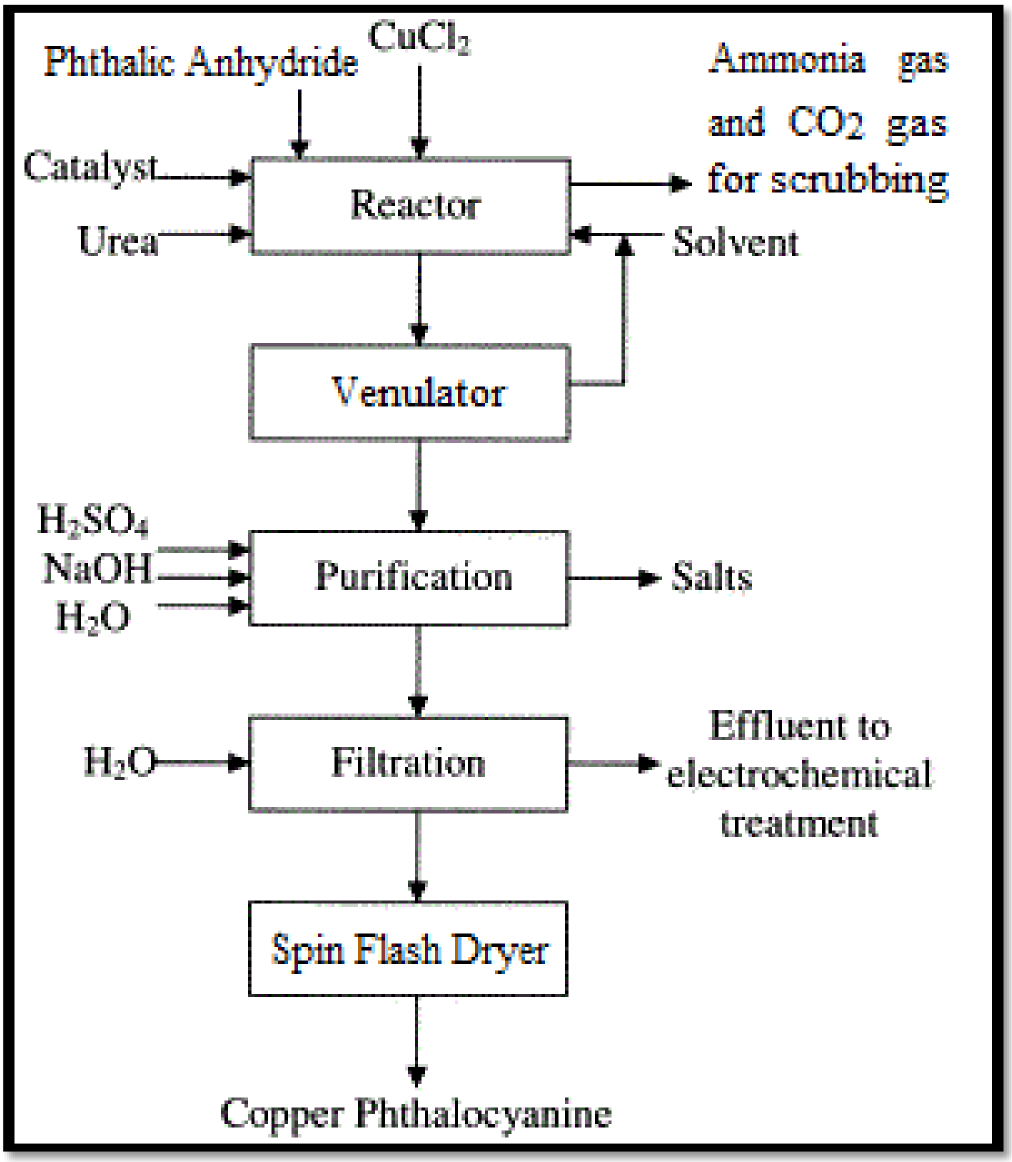

Figure 1:- Flow chart for the production of Copper phthalocyanine pigment (CPC Blue)

Stage I: Reaction

Crude copper phthalocyanine is produced by condensing phthalic anhydride, cuprous chloride and Urea in presence of ammonium molybdate as catalyst.

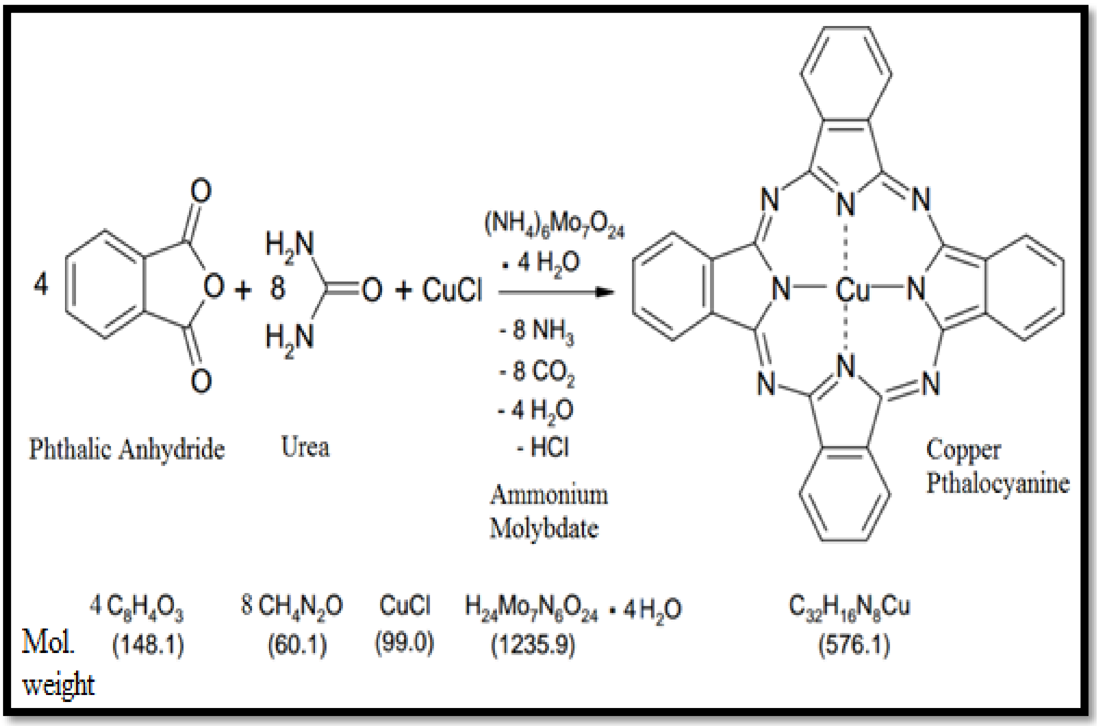

Figure 2:- Reaction for the manufacturing of Copper phthalocyanine [5]

In glass line reactor kettle having heating arrangement phthalic anhydride, cuprous chloride and Urea are charged. Tri-chlorobenzene is used as a solvent while ammonium molybdate is used as a catalyst. The reaction mass is heated to temperature of 180°C. During the reaction ammonia and carbon dioxide gas are evolved due to decomposition of urea, which are scrubbed in a two stage water scrubbing system.

Stage II: Solvent recovery

After the condensation reaction over, the product is transferred to venulator[1] for recovery of solvent, where Tri-chlorobenzene is distilled out using vacuum and crude copper phthalocyanine blue is obtained as cake.

Stage III: Acid purification

This crude product is then stirred with 15 % sulphuric acid and water. The mass is heated using live steam to 95°C. During the process, inorganic impurities get dissolved in water while the product, which is insoluble, remains in the solid form.

- In a process for purifying an unsubstituted or halogenated copper phthalocyanine by transforming it into its sulfate and recovering it by hydrolysis with water, the improvement comprising: introducing an unsubstituted or halogenated copper phthalocyanine into

  - A 4 to 10-fold amount of sulfuric acid of an initial strength of 84 to 88% by weight, or
  - A more concentrated sulfuric acid and diluting it to said concentration range, and heating the so-obtained copper phthalocyaninesulfate in an inert gas atmosphere to a temperature of 60° to 100° C.

- The phthalocyanine is dissolved first in concentrated sulfuric acid or oleum and then diluted by addition of water, to a sulfuric acid concentration of 84 to 88%.
- The crude phthalocyanine is introduced into 85.5 to 86.5% sulfuric acid.
- Heating is continued until the viscosity of the copper phthalocyaninesulfate suspension is strongly reduced.
- The halogenated copper phthalocyanine is a chlorinated copper phthalocyanine.
- The chlorine content is up to about 6% by weight.

Stage IV: Filtration

The slurry from the purification is taken to the filter press where the dissolved impurities are removed as filtrate, which is taken to the effluent treatment plant. The cake is then washed with water and the washings are also taken for treatment.

Stage V: Drying

The wet cake is then taken to the spin flash dryer[2]. The product obtained is a fine powder CPC Blue, which is then sent for packing.

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[1]Venulator: Here vacuum recovery of solvent takes place.

[2]Spin Flash dryer: A spin flash dryer produces powder from feed, which is viscous or gelatinous in nature, paste or filter cake.

MANUFACTURING OF INK FROM CRUDE POWDER:-

Once the copper phthalocyanine crude is formed, the next procedure is the manufacturing of the final product, that is, the thermochromic ink. The powdered form of crude is used for this. Following are the steps to be followed to carry out the experimental work

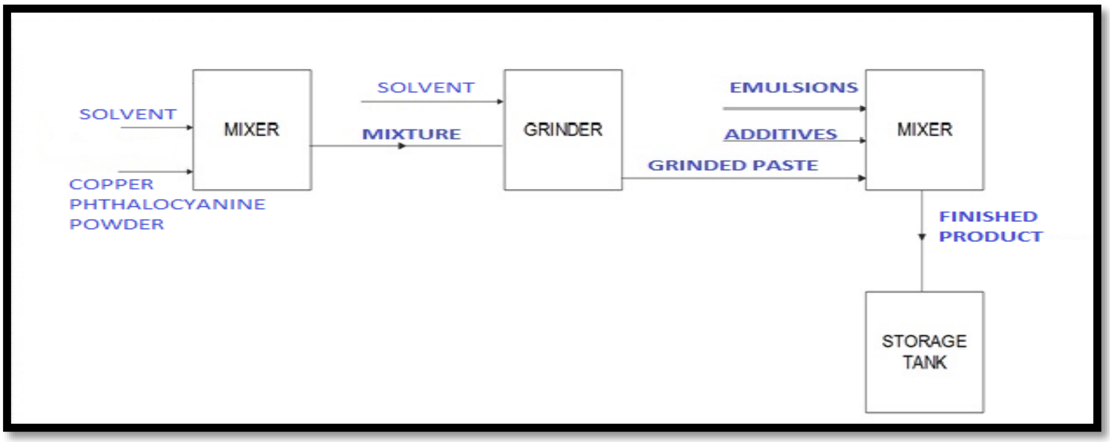

Figure 3:- Block Diagram for the manufacturing of Thermochromic ink.

STEP 1 MIXING

In a mixer, at standard temperature and pressure additives along with the copper phthalocyanine powder are charged. Ethyl alcohol- ethyl acetate solvent [6] (Approx. 75% of the total used in final composition) is added to the mixture in specific quantity. The mixture is then stirred and allowed to settle to form slurry.

STEP 2 GRINDING

After mixing, the above mixture is charged to the jacketed bead mill grinder [7] along with the solvent (the remaining 25% of solvent) to make a paste which is homogenous. The vessel, beads and sample are vigorously agitated by shaking and stirring. Water flows through the jacket to cool the grinding taking place inside as heat is generated. After the processing cycle, the beads settle by gravity in the vessel and the resulting homogenate is easily removed.During grinding, desired colour strength can be achieved by proper dispersion, wetting and stabilization of pigments. Manufacturing of ink is done by grinding in a resin solution containing carboxyl styrene-acrylic resin neutralised by the addition of ammonia, organic amine or alkaline hydroxide. These resin solutions provide good pigment wetting and pigment stabilisation. The continuous cost and performance optimisation has forced the ink manufacturers to streamline their production processes [8]. It is possible to save manufacturing costs by increasing the pigment content in the grinding stage. But doing this, negative side effects such as viscosity increase of the grind, even thixotrophy or reduced transparency and colour strength can occur. To avoid these, special pigment wetting and dispersing additives are developed that allow a significant increase of pigment loading without sacrificing the above mentioned properties. It may be interesting to note that such an additive can be used at relatively low dosages (1 to 3 percent) to display impressive effects. The additive used in this resin-containing carbon-black grind will be optimized with regards to its pigment wetting properties to have a positive impact on viscosity.It also contributes to pigment stabilisation, but most of this can be attributed to the high molecular weight resin solution. So the combination of a resin solution and a small amount of this rather low molecular weight pigment wetting additive achieves high pigment contents in the grind and excellent. Resin containing carbon black grind gloss, transparency and colour strength in without and with additional use of a wetting and the ink dispersing additive [8].

STEP 3 MIXING

This grinded paste along with emulsions and additives are charged into another mixer. The mixture is agitated and allowed to settle. This homogenous mixture is called Thermochromic ink. This is later packed in small containers and dispatched.

RESULTS AND DISCUSSION:-

The compositions of 6 samples are as shown in the table 1. The values of the properties are shown in the table 2. The values of these properties are found out by carrying out viscosity test, foam test and slip test. These tests were conducted at normal temperature and pressure. The range for the viscosity of the samples is between 25-47 Pa.sec, The pH is mostly neutral but 2 samples vary a bit. Since all the components remain the same, the density is constant. Because of the high % of solids, the viscosity is high which does not provide the dot gain[3] necessary and even the final cost of the product thus becomes high, therefore sample E is rejected and we choose sample A which has the viscosity and % solids in a mid-range that is optimum for the best production of the ink.We have studied all these properties to select the most optimum composition for the production of most economical product.From the results, Sample A is chosen for the final product. This sample was chosen because of the results of the foam test, viscosity test and slip test also the pH value and % solids are taken into account for the final product. Samples B, C, D and F have low values for almost all the properties, so they can be neglected. Although the slip test value and foam test value for sample E is higher than sample A, Sample E is neglected due to lower dot gain because of low viscosity.

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[3]Dot Gain: The degree of dot gain is an important factor in good print quality. If there is too much dot gain, the screen dot will print too wide, which in turn requires printing with a too low density.

Table 2:-

Different composition of ink

Components	Quantity (kg)					
Sample	A	B	C	D	E	F
Thermochromic blue Vicoat 1088	4.3	2.95	5.7	3.1	4.8	4
n- propyl acetate	1.6	0.95	0.05	1	0.5	1.2
Styrene acrylic emulsion 678	1	1.3	1.15	1.89	2	1
Micalman wax	1	1.5	1	1	0.7	1.7
DefoamerDC51	1	1.2	1	1.56	1	1
Resin Solution	0.05	0.6	0.05	0.9	0.4	0.05
Optical Brightener	0.05	0.7	0.05	0.05	0.3	0.05
Wetting & Dispersing Agent	1	0.8	1	0.5	0.3	1
Total	10	10	10	10	10	10

Table 3:-

Analysis of Different composition

Properties	Values					
Sample	A	B	C	D	E	F
Viscosity (Pa.sec)	40	30	25	42	38	32
pH	7.4	5	7	9	9	7.2
Density (kg/l)	1.02	1.02	1.02	1.02	1.02	1.02
% solids	35	28	35	31	47.5	32
% volatile	0.5	0.3	0.5	0.9	0.5	0.7
Foam test (hours)	48	30	43	37	53	39
Slip test (rubs)	170	100	165	120	200	135

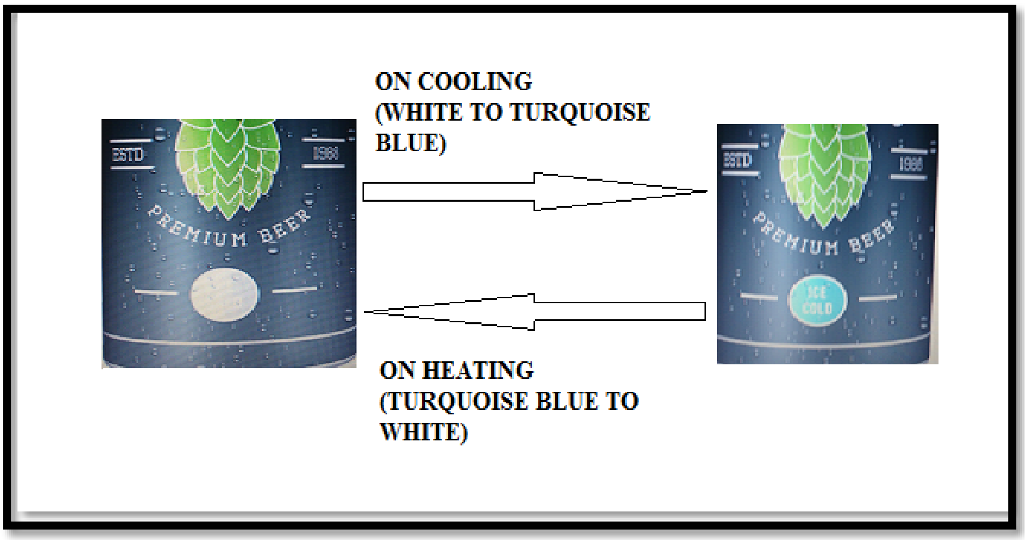

Figure 4:- Thermochromic ink colour change, depending upon the temperature.

CONCLUSION:-

The use of thermochromic inks is on the rise for ease in day to day life. There are not many methods to manufacture thermochromic ink but the optimum method and composition was studied and presented in this paper.

REFERENCES

[1]. Bamfield, P.; Hutchings, M G.: Chromic Phenomena: the technological applications of color chemistry, Royal Society of Chemistry, London, 2nded., chapters 1, pp.38- 47, **(2010)**

[2]. Kulcar, R.; Friskovec, M.; Hauptman, N,; Vesel, A,; Klanjseg M.: Colorimetric properties of reversible thermochromic printing inks, Dyes and pigments, Vol 86, Issue 3, pp. 271-277, **(2010)**

[3]. https://www.techwalla.com/articles/what-is-solvent-ink**(Last accessed on 28th Aug,2017)**

[4]. https://www.pcimag.com/articles/83452-copper-phthalocyanines **(Last accessed on 21st Sep, 2017)**

[5]. F. H. Moser, A. L. Thomas, Phthalocyanine Compounds, Reinhold, New York 1963; microwave application: A. Shaabani, J. Chem. Research (S) 1998, 672-673.**(1998)**

[6]. OSMAN SIMSEKER,**(2011)**," Investigation of Different Solvents in Flexographic Printing Ink's Effects to Print Quality on Coated and Uncoated Paper"Asian journal of Chemistry Volume 23, No. 7, 2903-2906

[7]. http://www.brancher.com/-Broyage-.html?lang=en **(Last accessed on 28th Aug, 2017)**

[8]. Article written by Heather Wansbrough from information supplied by Derek Taylor (Coates New Zealand). Extra information supplied by David Yuen with reference to:

- Kirk Othmer, Encyclopedia of Chemical Technology (3rd Edition), V.13 (374-397) & V.19 (110-175), Wiley & Sons, New York.**(1981)**
- Color index (3rd Edition), American Association of Textile Chemists and Colorists, London. **(1971)**