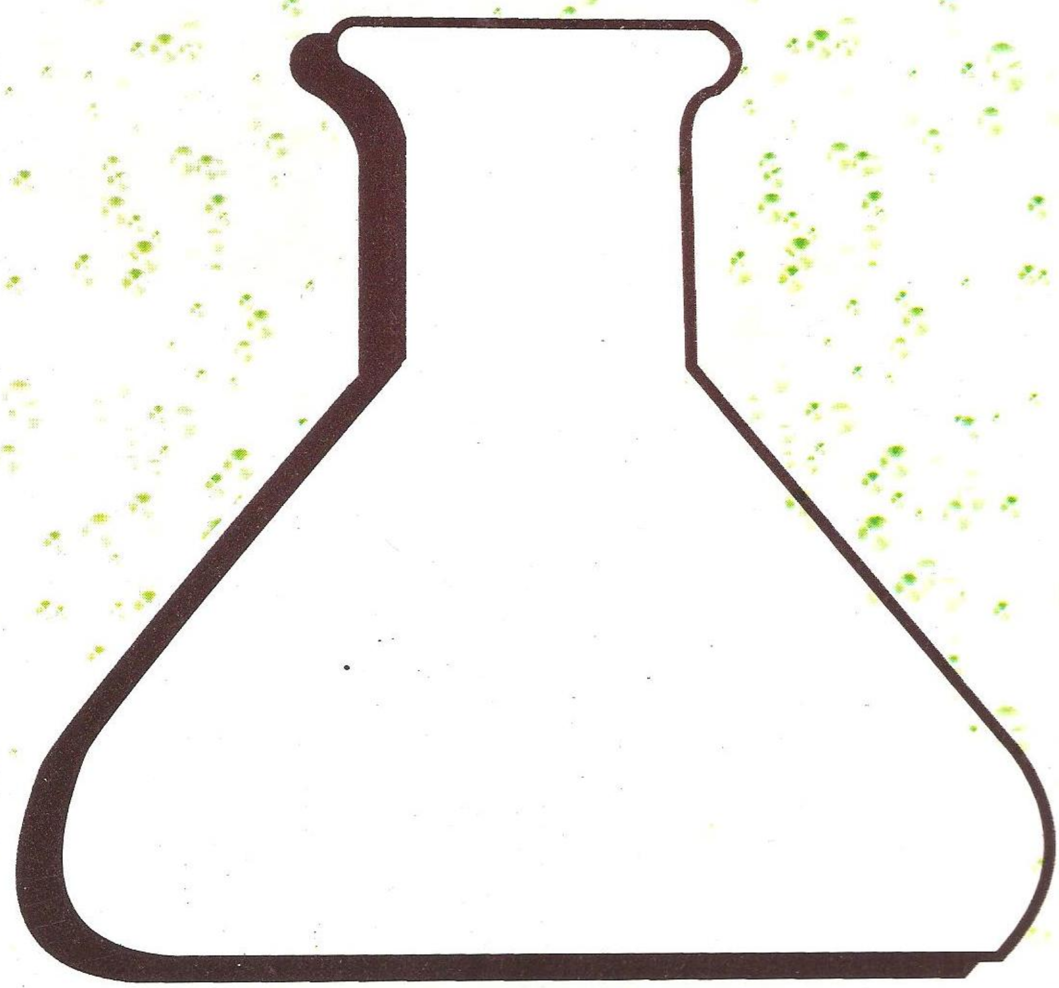
Bayero University, Kano

CHEMSEARCH Journal

ISSN: 2276-707X

CHEMICAL SOCIETY OF NIGERIA C.S.N

VOLUME 4 NO. 2 DECEMBER, 2013



Publication of Chemical Society of Nigeria Kano Chapter

c/o Department of Pure & Industrial Chemistry, Bayero University, Kano

ChemSearch Journal 4(2): 37 – 43, Dec., 2013
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 27/11/2013 Accepted: 09/12/2013

Preparation and Characterization of Water Based UV Curable Flexographic Printing Ink.

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ABSTRACT
Polyvinyl alcohol was utilized as a single sole binder in the formulation of water based UV curable flexographic printing inks. Six different formulation containing 2%, 3%, 4%, 5%, 8% and 10% polyvinyl alcohol were prepared using 1-(4-nitrophenyl)azo-2-naphthol as pigment and potassium dichromate as a cross linking agent. The formulations prepared were characterized for viscosity and FT-IR before being printed on different substrates. The ink films formed were assessed by optical microscopy, the print quality was found to meet most requirements in colour printing chemistry and technology applications.

Keywords: Flexographic printing inks, Pigment, Polyvinyl alcohol, Potassium dichromate

Introduction

Printing forms an integral and versatile position in our society as it is used to pass information and decorate objects. Flexography is a rotary printing method that applies fast drying fluid inks from simple inking system and prints from resilient plates of rubber or photopolymer that have the image in relief. The process is widely used to print packaging materials and product including corrugated boxes, folding cartons, multi walled sacks, plastics bags etc (Khodada and Farshad, 2011).

The print is a composite of ink(s) and substrate(s). Much has been achieved in recent times in the characterization of various type of surfaces typically used in printing processes. This surface features are of vital importance to the manner in which the thin ink film is received by the substrates (Guthrie and Lin, 1994). This film formed can be analysed or characterized by light microscopy (Svanholm, 2007, Salisu, 2012). Scanning electron microscopy (SEM) or by FT-IR, which gives broad depth resolution from 0.5-10,000nm with special resolution of 50micrometer. The main advantage of water based system lies in the elimination of organic solvent emission and removal of the need for solvent recovery or incineration. Pigment and dyes when included in UV light-curable formulations can influence the curing process in various ways (Guthrie and Lin, 1994).

Azo pigments are capable of coordinating to metals ion through one of the two azo nitrogen atoms utilizing its lone pairs in bonding (Christie, 2001). Using the alcohol solution with a lower surface tension improved the wettability and ought to make the absorption pattern less sensitive to the surface chemistry and more sensitive to the pore structure (Thorman *et al.*, 2012). In UV curing system containing metal complex, the absorption of light by metallic complexes can induce polymerization and or cross linking of the materials (Pizzocaro *et al.*, 2002, Maria 2004). When the ink is transferred to the substrate, three components interact: the image carrier, the ink and the substrate. The performance of the image carrier is to a large extent is influenced by its chemical, mechanical and physical properties. The solidification of the ink on the substrates is highly dependent on the ink-paper interactions (Johnson, 2008). This film formed can be analysed or characterized by light microscopy (Svanholm, 2007, Salisu, 2012).

In general, it is being observed that paste characteristics and film properties of polyester resin blend are better but because of economic reasons polyvinyl alcohol and acrylic polymers are preferred (Behera *et al*, 2008). Zolec-Tryznowska and Izdebska (2013) reported the preparation of flexographic printing ink modified with hyper branched polymers. The surface tension of the printing ink was measured and the rheological behaviour of the pure polymers and printing ink were presented. Results showed improved colour properties of the overprinted sample and colour fastness to rubbing due to the used of the hyper branch polymers. Khodada and Farshad (2011) reported the effect of ink and paper board characteristics on flexographic print quality based on print density and the result showed that solid content, pH and particle diameter of the inks influenced print quality.

To the best of our knowledge, there is no report in the literature where polyvinyl alcohol has been used as a single sole binder in flexographic printing ink formulation. But different application or in combination with PVA were mostly used.

Materials and Method

Materials

The chemicals and solvents used were of analar grade and were used without further purification. Polyvinyl alcohol 98% hydrolyzed (Merk Schuchardt), 2-naphthol (Titan Biotech), 4-nitroaniline (BDH), Sodium hydroxide (BDH), Sodium nitrite (BDH), Isopropanol (Sigma Aldrich), Propylene glycol (BDH), Potassium dichromate (BDH), conc. Hydrochloric acid (Sigma Aldrich), Methanol (Sigma Aldrich) and distilled water. All glass wares used were washed thoroughly with distilled water and dried in an oven, weighing was carried out on an electric balance model AB54. The infrared spectral analyses were recorded using Shimadzu 8400S IR spectrometer, while the photomicrograph of the image of the printed ink film was taken with digital light microscope camera AMSCOPE MD 900E (Svanholm 2007, Salisu, 2012).

Methodology

Synthesis of 1-(4-Nitrophenyl) azo-2-naphthol

4-nitroaniline was diazotized and Coupled with 2-naphthol at 0-5^{0}C in accordance with Daniel (2000). The resultant colourant obtained was recrystallized using methanol, dried and grounded into fine powder.

Preparation of polyvinyl alcohol solution

A Solution of 2% polyvinyl alcohol was made by in distilled water at a temperature of 85^{0}C with constant stirring until a clear PVA solution was obtained. The procedure was repeated for 3%, 4%, 5%, 8% and 10% polyvinyl alcohol solutions respectively.

Preparation of PVA printing ink formulations

Polyvinyl alcohol (160ml, 2%) solution was measured out and placed into a stainless steel bowl. The temperature was raised to 65^{0}C with stirring using designated stirrer at 250rpm and 10ml propylene glycol was added. The temperature was cooled down to 50^{0}C and 28g of 1-(4-nitrophenyl)-azo-2-naphthol (pigment) was dispersed slowly maintaining the speed of 250rpm for 20minute. Isopropanol (30ml) was added with continuous stirring at 160rpm, about 45ml water was added and stirred accordingly 4g potassium dichromate powder was then added slowly. The mixture was then heated at 40^{o}C for an hour using a digital water bath after which it was returned to ambient temperature to cool and then placed in an amber bottle. The procedure was repeated for 3%, 4%, 5%, 8% and 10% polyvinyl alcohol ink formulations, respectively. This method adopted was one reported by Sharma and Phan (1992) and specialized stirring equipment was designed for the purpose.

Results and Discussion

Physical Appearance of the formulated ink

The physical appearance of the formulated print ink were observed and was found that all the components were mixable and viscous, thereby produced a smooth red shaded dispersions of the ink.

Viscosity

The effect of viscosity of the water based inks on print quality of flexographic printing was investigated and found that reduction in ink viscosity reduced print quality. Increased viscosity of the ink formulation improved the maximum packing fraction (MFP) of the ink formulation which effectively supports the print quality.

The result of the viscosity measurement at 100rpm for spindle rotation of 3minutes at 40^{0}C was recorded in Fig. 1 below:

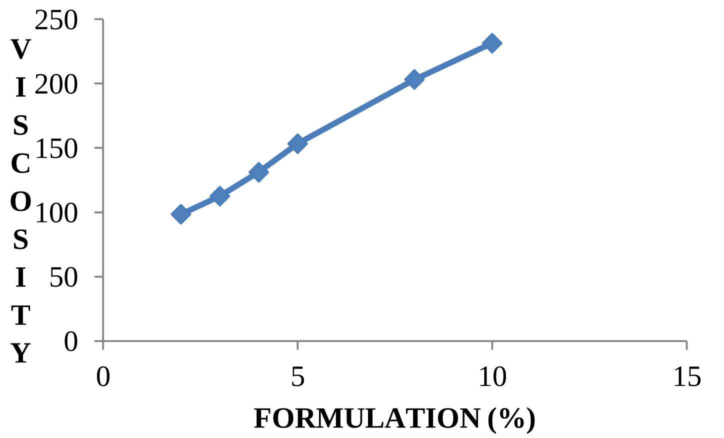


Fig. 1: Results of viscosity measurements (Values in centipoids cP)

It was observed that the viscosities of the formulae increased with increasing percentage of the binder, 2% formulation has lowest viscosity of 98.45cP while 10% formulation has highest of 231.41centipoise.

Fourier Transform Infrared spectroscopy (FT-IR)

The presence of important functional groups in the prepared ink formulations was resolved by observing selected bands in the FT-IR spectra obtained from the graph of transmittance (T%) against wave number (cm^{-1}) and the result recorded provide similar patterns throughout the samples.

Table 1: Result of the FTIR absorption bands for the formulations, PVA and Pigment.

Sample	ν (O-H)	ν(N=N)	ν(C-O)	ν(C=C)	ν(C-H)	ν(N-O)
A	3421.83	2105.51	1097.53	1643.41	2940.58	
B	3419.90	2106.34	1100.43	1643.41	2934.79	
C	3436.30	2104.41	1097.53	1646.30	2939.61	
D	3414.12	2105.37	1098.50	1643.33	2948.29	
E	1207.48	2429.42	--	1592.29	840.99	1323.21
F	3363.97		1096.57		2927.08	

KEY: A=2% ink. B=5% ink. C=8% ink. D=10% ink. E=Pigment. F=PVA

From Table 1 above the appearance of strong broad band due to hydroxyl stretching vibration for the samples (A,B,C,D and F) were observed In the region 3500– 3200cm^{-1}. This peaks appeared all through the series of these samples as they belong to the same category except for sample E with band in the region of 1207.48cm^{-1}due to aryl O-H bending vibration obtained at the range of 1390 -1180cm^{-1}. Bands in the region 2450 - 2100cm^{-1} were attributed to Azo (N=N) functional group except for sample F (PVA) which is absent in the spectra. Bands at 1260 - 1050cm^{-1} were due to strong C-O stretching vibration In the spectra of the samples except for sample E the pigment. Bands at 1620 - 1590cm^{-1} were assigned for aryl C=C stretching vibration except for sample F (PVA) which is absent in the spectra. Bands at 3000 - 2850cm^{-1} were due to C-H stretching vibration except for sample E with bands at 840.99cm^{-1} due to out of plane vibration for aromatic C-H present in the spectra. Bands at 1360 - 1290cm^{-1} were assigned for N–O symmetric stretching vibration of the nitro group present in the spectra of the pigment (E) and absent in the spectra of the ink formulation and the binder used in the preparation.

Film formation

The printed inks were assessed visually for film formation on the substrate as recognized by Sharma and Phan, 1992 and rated as Poor = 1 Fair = 2, Good = 3, Excellent = 4 and the result recorded in table 2 below:

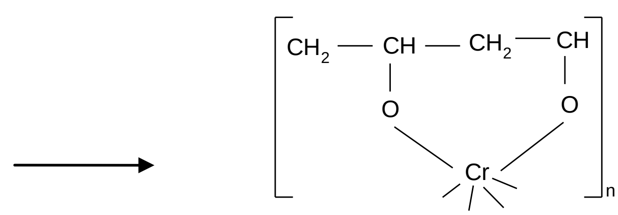
Table 2: Result of film formation of the formulae

Substrates	2% ink	3% ink	4% ink	5% ink	8% ink	10% ink
News print paper	2	2	3	3	3	3
Bond paper	2	2	2	3	3	3
Art paper	2	2	2	3	3	3
Packet carton	2	2	3	3	3	3
White cottonfabric	2	2	2	3	3	3
Aluminum foil paper	1	1	1	2	2	2

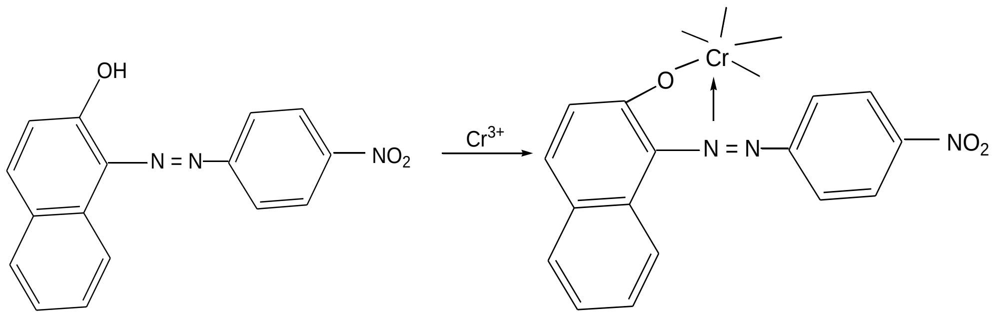
It can be seen from Table 2, that each formulation was found to have film formation of different grades on all the substrates, except for aluminum foil paper. The formation of good film by formulation containing 5%, 8% and 10% on art paper, bond paper, news print paper, packet carton and white cotton fabric (Table 2) may be attributed to the presence of polyvinyl alcohol which has good binding property and ability to form film. The formation of poor print on aluminium foil paper is due to inability of the water based printing Inks to wet the aluminium foil paper effectively. This poor film formation by formulation containing 2% and 3% PVA on the substrates is attributed to poor tackiness of the ink due to inadequate quantity of the polyvinyl alcohol as wetting of a paper surface by the ink is one of the basic requirements for ink absorption and ink transfer (Finch 1973).

Drying capacity and cross-linking

The formulae exhibited a high drying capacity, the rapid drying capacity exhibited by the formulae may be due to presence of potassium dichromate acting as a cross linking agent which formed a coordination bonds with polyvinyl alcohol and the pigment. Dichromate being a cross linking agent in these formulations and the presence of the required functional groups as presented in the FT-IR, it is essential that the following reactions were involved (Pizzocaro *et al*, 2002, Christie, 2001 and Kunjappu, 2001)

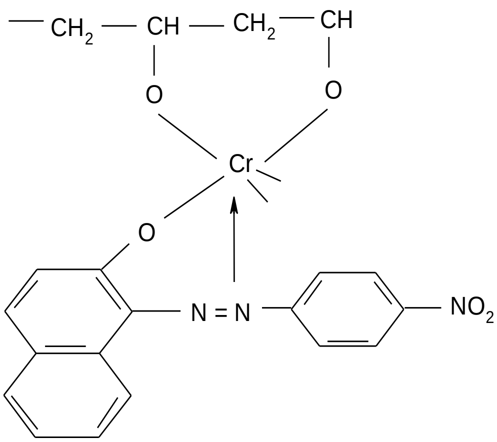


Cr (vi) + PVA^{+*} → Cr (v) + PVA$_{ox}$



Scheme 1: Chromium cross linking reactions.

Based on these reactions, the cured ink film would be expected to have the structure with chromium as a mordant as follows:



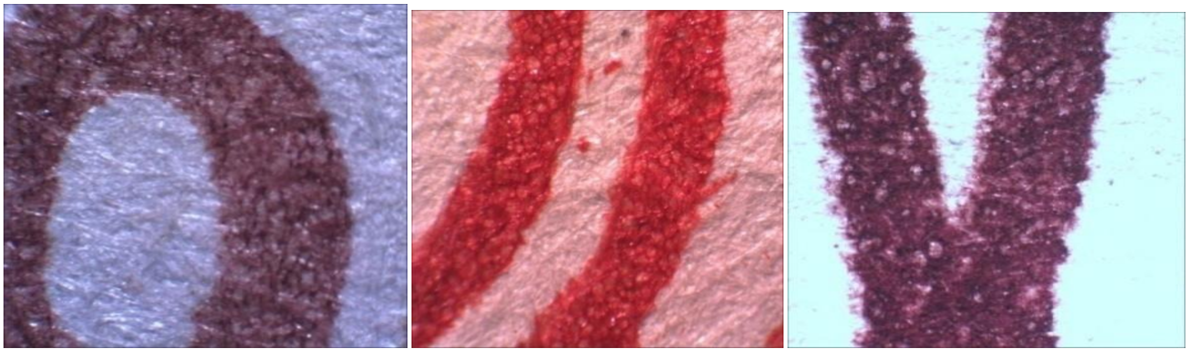
Scheme 2: Proposed structure of the printing ink

The remaining two vacant positions would be attached by the lower alcohol and/or printed substrate or trace water molecule which may remain in the dried/cross-linked ink film.

Printed Film Optical Microscopy

Fig. 2 showed the photomicrographs of a cross section of the ink film taken with digital light microscope camera (Amscope MD 900E) on news print paper Fig. 2a, bond paper Fig. 2b and art paper Fig. 2c, each for 5%, 8% and 10% ink formulations respectively.

The photomicrograph of a cross section of the dried/cross linked printed ink film of the formulations containing 5%, 8% and 10% on news print paper showed an even distribution of the pigment particles within the film with less or no air bubbles (Fig. 2a) where formulation of 8% showed better result. Bond paper showed good result with some air bubbles for the formulations (Fig.2b). In art paper which is smooth with less capacity to absorb more ink than news paper and bond paper, the printed film for the formulations showed much air space with uneven pigment particles distribution (Fig.2c).



5% /NEWS PRINT 8% /NEWS PRINT 10% /NEWS PRINT

Fig. 2a photomicrograph of a cross section of the printed ink film on news paper

5%/BOND PAPER 8%/BOND PAPER 10%/BOND PAPER

Fig. 2b photomicrograph of a cross section of the printed ink film on bond paper

5%/ART PAPER 8%/ART PAPER 10%/ART PAPER

Fig. 2c photomicrograph of a cross section of the printed ink film on Art paper

However, 8% formulation exhibits, better adhesion with better particle distribution for the film as observed on news print papers, bond paper and art paper under this test condition. These optical film photomicrographs results are comparable with one reported by Svanholm, 2007. With increasing demand to reduce the problems caused by volatile organic compounds (VOC), the new solution in printing chemistry and technology is now turned on water based inks with energy curing products. Thus, formulation of different percentage compositions of PVA based flexographic printing ink that offered low solvent retention for reduced odour in the final print, single ink system for multiple structures, good print properties on various substrates and finally environmentally friendly. This shows that polyvinyl alcohol forms enormous cross-linked networks with the pigment within the film after UV light irradiation because of their superior photosensitivity.

Conclusion

Poly(vinyl alcohol) can be utilized as sole binder in flexographic printing applications. The 5%, 8% and 10% formulation formed on art paper, bond paper, news print paper, packet carton and white cotton fabric. The formation of poor print on aluminium foil paper was due to inability of the water based printing Inks to wet the aluminium foil paper effectively. The ink formulation could be satisfactorily used for news paper printing, board, paper board, coated and uncoated paper and other printing services involving the use of paper materials for packing industry. More research work shall be carried out to improve the quality of the formulation as well as deinkability of the formulation.

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