Preparation and Application of Polyvinyl Alcohol Based UV Curable Flexographic Printing Ink

A. A. Salisu, H. Abba, M. S. Inuwa

Abstract **Polyvinyl alcohol was utilized as a single sole binder in the formulation of water based UV curable flexographic printing inks. Six different formulation composition 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 integrity and pigment particle distribution of the ink film formed were assessed by optical microscopy, the print quality and fastness properties were found to meet most requirements in colour printing chemistry and technology applications.**

Index Terms**: Poly(vinyl alcohol), Pigment, Flexography, Binder, Printing ink**

I. INTRODUCTION

Flexography is a rotary printing method that applies fast drying fluid inks from simple inking system and prints to resilient plates of rubber or photopolymer that have the image in relief [8]. The process is widely used to print packaging materials and product including corrugated boxes, folding cartons, multi walled sacks, plastics bags etc [1]. Water based flexographic inks introduced in the 1930s achieved significant commercial use in paper and paperboard printing during the 1950s and 1960s, and are today used in almost all areas of flexographic printing. The regulatory factors especially during the 1980s, with its high pressure on safety and environment, were an important driving force for the further development of water-based technology [11]. This technology continues to advance at the expense of solvent-based inks. Radiation curing inks, such as UV- and EB-curable (electron beam), are also widely used and are an increasing market [2]. Binders are used primarily to bind coating pigment together and to anchor the coating to the substrate [3].

Pigments and dyes when included in UV light curable formulations can influence the curing process in various ways. For examples, it can have marked effect on the storage stability of the inks, on the resilience of the cured assembly and, as would be expected, on the formation/rheological properties of the formulation [5].

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Suitable organic colourants or pigments may include but not limited to azo, quinacridone, benzimidazole, indolines, quinophthalone derives or inorganic pigments such as titanium dioxide, iron red, carbon black etc [6]. The formulation can influence the properties of the pigment as well.

Polyvinyl Alcohol has been the largest volume of synthetic water-soluble resin produced in the world [7]. The excellent chemical resistance and physical properties of PVA resins have resulted in broad industrial use as an excellent adhesive and posses solvent, oil and grease resistance properties matched by few polymers. Polyvinyl alcohol films exhibit high tensile strength, abrasion resistance and oxygen barrier properties which under dry condition are superior to those of most polymers. The polymer's low surfaces tension provide for excellent emulsification and protective colloid properties [7]. The most commonly used binders in receptive coatings are polyvinyl alcohol or starch both with good binding strength and proven high impact on colour gamut. However, the polymer film formed by polyvinyl alcohol or starch may be enhancing due to good film forming characteristics observed by light microscopy and ESCA.ESEM analysis [8]. 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. Pigments and dyes when included in UV light-curable formulations can influence the curing process in various ways [5]. Azo group containing pigments are capable of coordinating to the metals ion through one of the two azo group nitrogen atoms utilizing its lone pairs in bonding [8]. 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 [10]. In UV curing system containing metal complex, the absorption of light by metallic complexes can induce polymerization and /or cross linking of the materials [11].

The solidification of the ink on the substrates is highly dependent on the ink-paper interactions [12 and 15]. In general, it was observed that paste characteristics and film properties of polyester resin blends are better but, because of economic reasons polyvinyl alcohol and acrylic polymers are preferred. Zolec-Tryznowska and Izdebska (2013) [18] 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 studied. The result showed improved colour properties of the overprinted sample and colour fastness to rubbing. Khodada and Farshad (2011) [1] 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 reported as stated earlier. A lot of research works were carried out on flexographic printing inks and the use of polyvinyl alcohol in related applications.

II. MATERIALS AND METHOD

A. 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-nitro aniline (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 analysis were recorded using Shimadzu 8400S IR spectrometer, light fastness was recorded using light fastness tester MK1 fitted with mercury tungsten (MBTF) 500watt lamp. The abrasion resistance determined using Sutherland rub tester while, the photomicrograph of the image of the printed ink film was taken with digital light microscope camera AMSCOPE MD 900E according to method reported by [8].

B. METHODOLOGY

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

Exactly 30ml of water was placed in 250ml beaker and 30ml of conc. hydrochloric acid added and settled in an ice bath. 4-nitroaniline (14g, 0.101M) was weighed and placed in 500ml beaker, 7.6g of sodium nitrite ($NaNO_2$) and 30ml distilled water added respectively and stirred thoroughly with a glass rod. The suspension was quickly added to the ice cold HCl solution using Pasteur pipette and kept in the ice bath and the mixture stirred with a glass rod while making this addition. After this addition was completed stirring was done occasionally for 10minutes [3 and 16].

ii. Coupling reaction

2-Naphthol (16.32g, 0.102M) was placed in 500ml flask followed by 200ml of 2.5M NaOH solution and the mixture was placed in an ice bath (0-5^{0}C). The solution of diazonium salt was then added to the solution of coupling agent drop wise with stirring, the reaction mixture was allowed for 10 minutes in the ice bath. The colour change from yellow to red was noted. 20g of NaCl was added to the mixture and heated to boil on a hot plate, then removed, cooled to room temperature and placed on ice bath. The solid precipitate was filtered by vacuum filtration using Buchner funnel, washed with 80ml NaCl solution twice and recystallization using methanol, filtered and then dried in air. The solid crystals were then grinded and a very fine powder was obtained [3 and 16].

iii. Preparation of polyvinyl alcohol solution

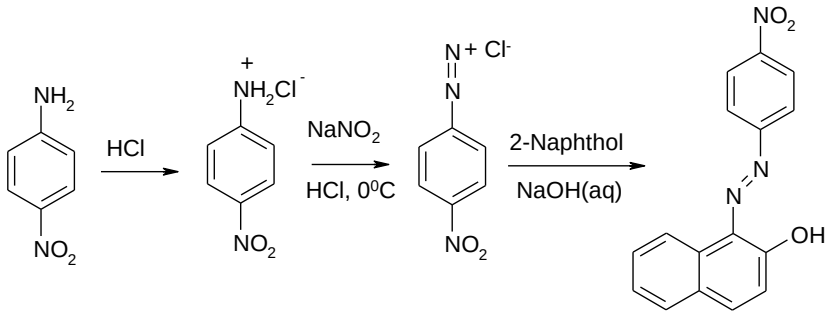
Solution of 2% polyvinyl alcohol solution was made by weighing 6g, of polyvinyl alcohol, and dissolved in 300ml distilled water by heating to the temperature between 85-95^{0}C with constant stirring until a clear PVA solution was obtained. The procedure was repeated each for 3%, 4%, 5%, 8% and 10% polyvinyl alcohol solution respectively.

iv. Preparation of 2% PVA printing ink

Exactly 160ml /130g, of 2% polyvinyl alcohol solution was measured out and placed into a stainless steel bowl. The temperature was raised to 65^{0}C with stirring using designed 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 and then 30ml isopropanol was added with continuous stirring at lower speed of 160rpm. 45ml water added and stirred accordingly 4g potassium dichromate powder was dissolved in 45ml water and then added slowly with continues stirring. The mixture was then heated at 40^{0}C for an hour using a digital water bath after which it was returned to ambient temperature to cool and then placed in amber bottle. The procedure was repeated each for 3%, 4%, 5%, 8% and 10% ink formulations respectively according to the method reported by [14].

C. RESULT AND DISCUSSION

Scheme **1** illustrates the structures and the synthetic route to the pigment (1-(4-Nitrophenyl) azo-2-naphthol). It was prepared by diazotization of 4-nitroaniline and then coupling of diazonium salt, with β-naphthol yielding 1-(4-Nitrophenyl) azo-2-naphthol **2** according to [16].



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

i. Viscosities

The viscosity of the formulated ink was measured using rotating viscometer Brookfield type DV-E viscometer model. The measurements were carried out without spindle guard leg in 250ml beaker at 100rpm for 3 minutes at 40^0C and the result obtained is presented in Fig.1. The effect of viscosity of 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 [5 and 18].

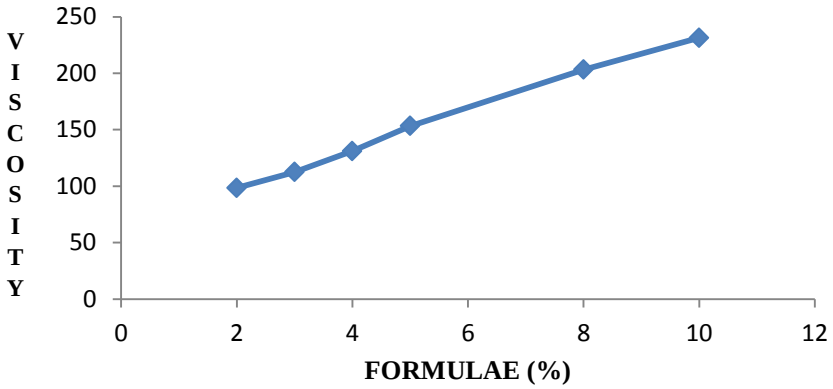


Fig. 1: Results of viscosity measurements (Values in centipoids cP)

The result of the viscosity measurement at 100rpm for spindle rotation of 3minutes at 40^0C was recorded in Fig.1. It can be 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 231.41 centipoids. This may be due to increase in percentage composition of PVA for its viscosity formation behavior [17] and effect of viscosity of water based inks on print quality of flexographic printing was investigated and found that reduction in ink viscosity reduced print quality [1].

ii. 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 the 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.

iii. Film Formation

The formation of good film by formulation containing 5%, 8% and 10% on art paper, bond paper, news print paper, packet carton and white fabric (Table 1) may be attributed to the presence of polyvinyl alcohol which has good binding property and ability to form film.

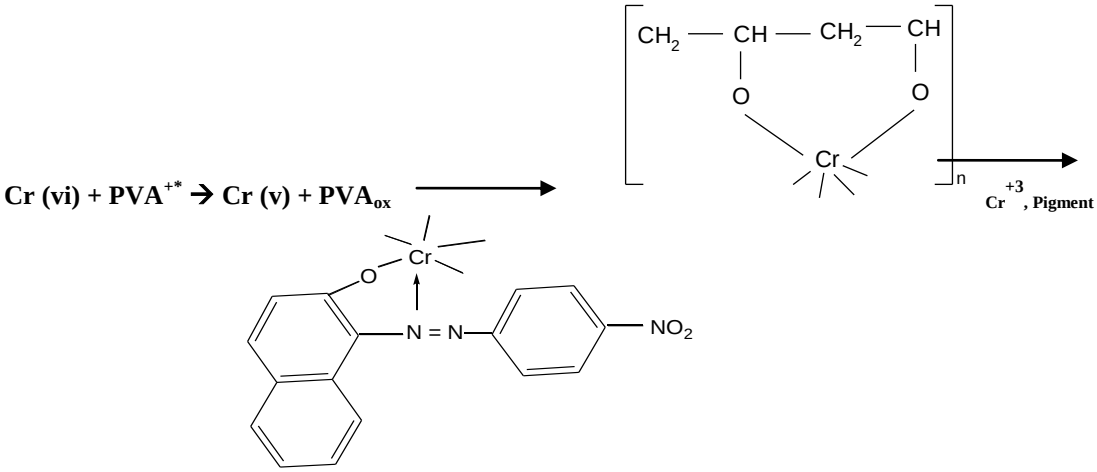
Table 2: Result of film formation of the formulae on different substrates

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 cotton	2	2	2	3	3	3
Aluminum foil paper	1	1	1	2	2	2

From table 1, it can be observed that each formula was found to have film formation of different grades on all the substrates, except for aluminum foil paper. The poor film formation by formula containing 2% and 3% formula on the substrates was attributed to poor tackiness of the ink due to inadequate quantity of the polyvinyl alcohol. The formation of poor print on aluminium foil paper may be due to inability of the water based printing Ink to wet the aluminium foil paper effectively.

iv. Drying Capacity

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 form a coordination bonds with polyvinyl alcohol and the pigment as in scheme 2 and 3 [9]. 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 reaction was involved [11 and 9].



Scheme 1: Chromium cross linking reactions.

v. Light Fastness

From table 2, it can be seen that light fastness property exhibited by the formula containing 2%, 3% and 4% were within the range of 3 and 4 for all the substrates except for 4% formula on news print paper which is 5 and aluminum foil paper which was undetectable due to the inability of the water based ink formulation to form good film on it.

Table 2: Light fastness properties of the formulae on various substrates.

Substrates	2% ink	3% ink	4% ink	5% ink	8% ink	10% ink
News paper	4	4	5	6	6	6
Bond paper	3	3	4	5	5	5
Art paper	3	3	3	3	5	5
Packet carton	3	4	4	6	6	6
White cotton fabric	3	4	4	5	5	5
Aluminum foil paper	-	-	-	3	3	3

5%, 8% and 10% formula exhibited good light fastness properties in the range of 6 for news print paper and packet carton, whereas the fastness on other substrates were within the range of 5 correspond to the 4% ink formulation on news print paper. While aluminum foil paper were at the range of 3 due to inconsistent film formed.

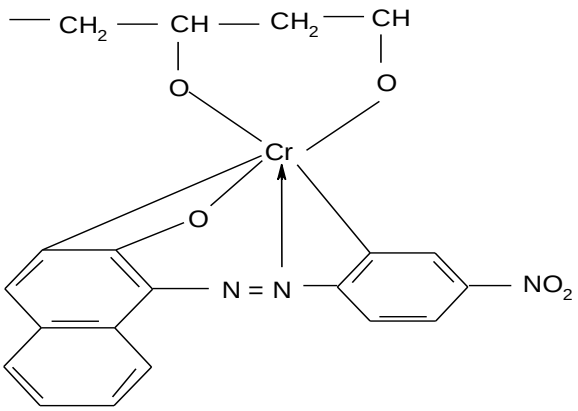
vi. Wet/Water resistance

The wet/water resistance property of the printed ink film for each formula was determined by water spot test, according to the method described by [14]. From Table 3, it can be seen that formula containing 5%, 8% and 10% relatively showed an acceptable resistance on all the substrates except for aluminium foil paper and 5% formula on art paper which were rated fair.

Table 3: Result of wet/water resistance of the various substrates printed with the ink 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	1	1	1	2	2	2
Packet carton	2	2	2	3	3	3
White cotton	2	2	2	3	3	3
Aluminum foil paper	1	1	1	2	2	2

The good wet resistance property exhibited by the formulae may be due to cross linking of the ink film due to UV light irradiation resulted in Cr^{3+} ion and PVA network insoluble in water by bridging reactions [9]. The formulation containing 2% and 3% PVA showed fair resistance on all the substrates except for Art paper and aluminium foil paper which was generally very low due to poor adhesion of the ink to the aluminium substrate. Where, 4% was found to be intermediate. The poor wet resistance on aluminium foil paper was attributed to poor film formation of the prints resulted due to inability of the ink to effectively wet the substrate. Azo pigments are capable of coordinating to the metals ion through one of the two azo nitrogen atoms utilizing its lone pairs in bonding [9] as in scheme 2 and 3 below**.** Based on these reactions, the cured ink film would be expected to have the structure with chromium as a mordant as follows



Scheme 3: Proposed structure of the printed ink film

vii. Abbrasion/Rub resistance

Table 4 present the data obtained for abrasion/Rub resistance. It can be observed that 5%, 8% and 10% formulae showed good to excellent dry rub resistance on all the substrates except for aluminum foil paper and 5% formula on art paper which is fair.

Table 4: Result of the Abrasion/dry rub resistance of ink formulae printed on different substrates:

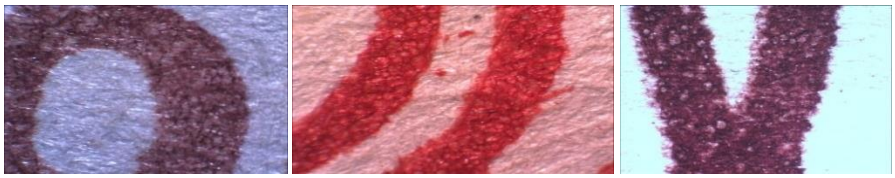
Substrates	2%ink	3% ink	4% ink	5% ink	8% ink	10% ink
News print paper	2	3	3	4	4	4
Bond paper	2	3	3	3	4	4
Art paper	1	1	2	2	3	3
Packet carton	2	3	3	3	4	4
White cotton fabric	2	3	3	4	4	4
Aluminium foil paper	1	1	1	2	2	2

The ability of pigment particles to hold mechanically within the polymer matrix [13] (Parker, 1992) and the ability of the PVA based printing ink to wet these substrates permitting good adhesion [6 and 12].

viii. Printed Film Optical Microscopy

The photomicrograph of a cross section of the ink film taken with digital light microscope camera (Amscope MD 900E) of the surface scanned under light stereo microscope for the film printed on news print paper, bond paper and art paper Fig. 2a, each for 5%, 8% and 10% ink formulations respectively.

The photomicrograph of a cross section of the dried 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 where, formulation of 8% showed better result (Fig. 3). Bond paper showed good result with some air bubbles for the formulations. 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. 3). 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

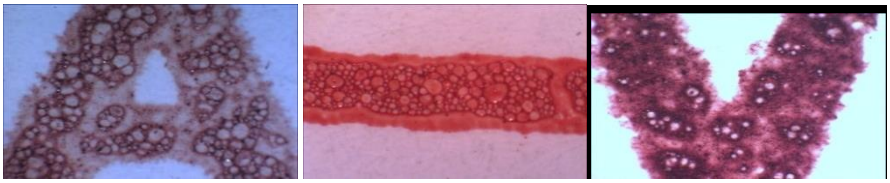


5% /NEWS PRINT 8% /NEWS PRINT 10% /NEWS PRINT

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

These optical film photomicrograph results are comparable with one reported by [8]. The physical appearance of the formulated formulae were mixable and viscous, thereby produced a smoothed red shade dispersion of the ink.

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. Utilization of poly(vinyl alcohol) as a sole single binder with 1-(4-nitrophenyl)azo-2-naphthol pigment under the influence of potassium dichromate as UV cross linking agent in which the mechanical properties including hardness, strength and adhesive force of the ink film increased with increase of the binder, because the cross linked density of the UV film increases with content of the binders (PVA) terminal group from sample containing 5%, 8% and 10% respectively. 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 form enormous crosslink networks with the pigment within the film after UV light irradiation because of their superior photosensitivity [9].

D. 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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