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**Article:**

Abd El-Wahab, H, Meligi, GA, Hassaan, MG et al. (1 more author) (2020) New water-based flexographic ink based on new ter-polymer nano-particles as eco-friendly binders – Part II. *Pigment & Resin Technology*. ISSN 0369-9420

<https://doi.org/10.1108/prt-12-2019-0111>

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# **New water-based flexographic ink based on new ter-polymer nano-particles as eco-friendly binders - Part II**

## **Abstract**

**Purpose** - The purpose of the study that is reported in this paper was to prepare, characterise and evaluate nano-emulsions of ter-polymers of various compositions as eco-friendly binders for flexographic ink industry.

**Design/methodology/approach** - Various nano emulsions of ter-polymers were prepared based on (VAM), Vinyl Versatate (VeoVa10®), butyl acrylate (BuAc), acrylic acid (AA) and acrylamide (AAM) monomers by means of a conventional seeded emulsion polymerisation technique, using  $K_2S_2O_8$  as the initiator. The characterisation of the prepared emulsions was performed using FT-IR, TGA, GPC, and TEM. A selection of co-polymers and ter-polymers were formulated with pigments and additional ingredients, as water-based flexographic inks. The inks were characterised for their rheological properties, pH, degree of dispersion, water resistance, and colour density.

**Findings** - It was found that the low viscosity of the prepared polymers may reduce the film thickness of the flexographic inks and may also increase the spreading of the ink on the surface. As a result, stable modified poly acrylate-based latex with improved physico-mechanical properties were obtained. The prepared latexes showed improved properties such as enhanced thermal stability and better water resistance. The effect of the emulsifier type on the properties of the resulting emulsion latexes, and their corresponding films, were investigated. Also, as the hydrophobic monomer increases, so does the colour density, and increasing the binder ratio enhances the gloss values. The improving in gloss values) were obtained and provide excellent adhesion properties for both the pigment particles and the base paper.

**Research limitations/implications** - The study focuses on the preparation of new water-based ter-polymer nano-particles and their use as eco-friendly binders for flexographic ink industry. Ink formulations based on other different type emulsion polymers could also be studied in order to assess the applicability of the ink formulation system found for other binders.

**Practical implications** - The ink formulations developed could find use in industrial scale printing.

**Originality/value** - Eco-friendly environment and low cost ink formulations for printing on paper substrates are novel.

**Keywords:** Acrylate ter-polymers, nano-emulsion, water-based inks, flexographic inks, eco-friendly binders

## **Introduction**

Flexography or flexo printing can be described as rotary relief printing process, in which the image carrier is a photopolymer plate or a flexible rubber with raised image areas. The quality of flexographic printing has improved dramatically as a result of improvements to printing plates, ink systems and especially inking units (such as anilox and doctor blade system). The majority of printers are moving towards using water-based systems, however, widely known that most of the properties of solvent-based inks are superior to those of water-based inks (Hamroush and Lin, 2012). The ink industry is one of the world's growth markets, due to the increasing demand for printing inks for packaging applications (Izdebska, 2016). Recently, print quality aspects to ink penetration of water-based flexographic ink into calcium carbonate based coatings of differently engineered structures was studied and evaluated (Bohlin, 2013). Inks are generally made of four major components; binders, pigments, solvent (or dispersion media) and a variety of property enhancement additives. Based on their compositions, inks may be classified into two categories namely, solvent-based inks (formulated using volatile organic compounds as solvents) and water-based inks (formulated using water as the solvent). The presence of volatile organic compounds in solvent-based inks makes their use less environmentally friendly than water-based inks. This has led to the increase in demand for water-based inks (Zolek, 2015). Water-based printing inks have been successfully used in different printing applications on various surfaces or substrates (Izdebska, 2016). Previous studies have shown that the type and amount of different components used in the formulation of printing inks, such as the polymer binders, have effects on the properties of the ink (Pekarovicova, 2016). There are also studies that show that different additives improve the print properties of water-based ink formulations (Zolek, 2015). The three additives generally used in water-based ink formulations are: (1) surfactants, (2) defoamers and (3) waxes. Surfactants are added to reduce the surface tension of water-based inks to allow adhesion onto non-porous substrates. The inclusion of surfactants in ink formulations however results in the creation of a stable foam during mixing (Leach, 1988). Water-based ink formulations containing wax, surfactant, and defoamer additives were prepared and printed on polyethylene film substrates. Standard test methods for adhesion, rub resistance, and gloss were undertaken on the printed polyethylene films. Quantitative image analyses were undertaken to quantify adhesion and rub resistance. Quantitative measurements were also carried out to quantify gloss (Carlo, 2018). Water-based ink (Wang, 2011; Pang, 2014; Gong, 2014) mainly comprises the following components: starch, deionised water, sodium hypochlorite, sodium hydroxide (Yang, 2014; Li, 2014; Chen, 2008), polyvinyl alcohol, urea, nickel sulphate, colorant and auxiliary agents. Auxiliary agents include defoamers, driers and surfactants. Water-based inks are considered environmentally friendly within the packaging industry, and yet the water-based inks currently used for printing still have notable disadvantages *i.e.* the complicated preparation process and high cost, of a single use, water-based ink and pigment and printing method. A recently patented water-based ink claimed to have solved these problems. In view of these problems, recent patents have also claimed to improve the adaptability of water-based inks (Zheng, 2016; Niu, 2016; Xu, 2015), via the printing method and the type of pigment used. Water-based inks have the advantage over solvent-based inks in that they are non-toxic,

odourless and non-polluting with respect to the environment. The inks are claimed to have good bonding properties and their application is very broad *i.e.* they can be used for screen printing, flexography and gravure printing. There is adaptability with respect to pigment type and dyes can also be added. Flexographic printing is widely used for packaging applications and the properties required of the print to be fit for purpose, with respect to the range of packaging applications and storage conditions can be extremely diverse. Tests can be devised for ink and print to simulate the various conditions of use, and under ideal circumstances a specification is drawn up between the packer, converter and ink-maker to agree on test methods and standards which are acceptable to all. The best way to speed up drying is by applying a lower film-weight of ink. As water inks give rapid viscosity reductions on dilution, this will allow high solids-strength at printing viscosities without compromising the print strength. The adhesion and flexibility of water-based inks to impervious substrates is controlled by the selection of the polymer emulsion (Leach, 1993). The key objective for coating paper and paper board is to improve their aesthetic appearance and printability. Coatings offer smoothness, gloss, brightness, and opacity to the base papers and provide them with enhanced printability, which requires resistance to ink splitting forces, smoothness, ink hold-out and gloss etc. The reason that latex is widely used as a pigment binder in paper coatings is that it overcomes many dilemmas such as binder migration, print mottle, blister, water retention and varied coating rheology (El-Sherbiny, 2014). Semi-continuous emulsion polymerisation, hetero-phase polymerisation with reactive surfactants, or by non-seeded semi-batch emulsion polymerisation, were carried out for different applications for this type of copolymer, such as binders for flexographic printing inks (El-Sherif, 2017). Coated papers have an excessive impact on the appearance and utility of printed materials with respect to the increase in mechanical strength, print gloss and print density. Styrene-butyl acrylate copolymers were synthesised utilising different emulsifier systems and modified with acrylamide (El-Sherif, 2018). New water-based ink, using acrylate co- and terpolymers as binders, were prepared and evaluated. The hydrophobic alkali-soluble emulsion (HASE) was prepared using a semi-batch emulsion polymerisation technique and evaluated as a binder for water-based printing inks (Abd El-Wahab, 2019). It is essential for good printability of the ink, especially in flexographic and gravure printing at high press speeds that the printing process is run without the ink drying in the gravure cylinder cell. In water-based emulsion polymer, however, the film formation process proceeds in a different manner and this adversely influences reversibility. In addition to good reversibility, HASE exhibits excellent ink properties such as good pigment wetting, excellent compatibility and a low minimum film forming temperature (Peters, 2001).

The research reported in this manuscript focused on improving the mechanical and physical properties of flexographic printing ink by using the prepared acrylic copolymers and terpolymer nano-emulsions, with different types of surfactant. A selection of the copolymers and the terpolymers were formulated with the presence of pigments, and other ingredients, to give water-based flexographic inks, which were then characterised. The key aim of this work was to prepare stable co- and terpolymers based on acrylic monomers by an emulsion

polymerisation technique, to be used in the preparation of water-based flexographic inks.

## **Experimental**

### **Materials**

Vinyl acetate (VAM), Vinyl Versatate (Veova10®), butyl acrylate (BuAc), acrylic acid (AA) and acrylamide (AAM), supplied by Sigma-Aldrich Company, USA, were used as essential monomers. Potassium persulphate (KPS), sodium acetate, nonylphenol ethoxylate (NP30) and sodium lauryl sulphate (SLS) were supplied by Sigma-Aldrich Company, USA. Sodium salt of fatty alcohol sulphate (supplied by Cognis, GmbH under the trade name SULFOPON 12 G) was used as an anionic emulsifier. Anti-fungi (VINYZENE IT-4000 DIDP), dipropylene glycol methyl ether (Dowanol DPM) and anti-microbial (DOWICIL QK-20), used in this research, were supplied by the DOW Chemical Company. JONCRYL90 used was imported from BASF Chemical Company. The wetting agent Surfynol 104 was imported from Muzing Company and the anti-foaming agent BYK 037 was provided by the BYK Company. Polyethylene wax used was produced by the Johnson Polymer Company and the Eljon Red 2RXs (yellow shade red pigment), the Barium Lithol Red (C.I. Pigment Red 49:1), and the DCC Pink Fb (blue shade red copper ferrocyanide pigment) were imported from the DCC Chemical Company.

### **Procedures**

#### *Pre-emulsion*

First of all, The distilled water and the emulsifiers were mixed with the monomers (VAM, BuAc and Veova10) to prepare the terpolymer. All of this raw materials put into the flask equipped with the high-speed homogeniser for 30 minutes (in three time portions). The acid monomer (Acrylic acid) is added during mixing, this step named pre-emulsion.

#### *Emulsion polymerisation of VAM, Veova 10 and BuAc, ter-polymer (Ahmed, 2017)*

The co-polymerisation of VAM, Veova 10 and BuAc, was carried out in a water bath, with the material being refluxed in a 1000ml three-necked flask equipped with a stirrer and having a gas inlet system. Oxygen was removed by purging nitrogen through the mixture for at least 30 minutes. Then, 80.5 ml of distilled water was introduced into a glass reactor with 2.2 g sodium lauryl sulphate (SLS) and SULFOPON 12 G as anionic surfactants. Then, 0.4 g of NP30 non-ionic surfactant was added and this was followed by 8 ml of distilled water and 0.1 g of potassium persulfate (KPS) as the initiator. The mixture was stirred under nitrogen atmosphere at 80°C. The SLS dissolved in distilled water (2.2 g in 59.6 g), was then mixed with different ratios of VAM, Veova 10 and BuAc, according to polymer type, using vigorous stirring with the homogeniser at room temperature for 30 min. The 10% of obtained pre-emulsion was charged into the reactor for 30 minutes as a seeding stage, and then there was a 30 minutes wait before the 0.1 g KPS initiator, dissolved in 17 ml distilled water, was gradually added. The 2%AA and the 0.4 NP30 were mixed with the remaining 90% pre-emulsion, using the homogeniser, and this was charged into the reactor within a 3 hours period. The reaction was allowed to proceed under continuous stirring at 80 rpm and then the temperature was raised to 83 °C. At the end of

the pre-emulsion addition, the temperature was raised from 83 to 85 °C for 1 hour to complete the polymerisation reaction. The prepared emulsion was then cooled to 40 °C and the pH adjusted to pH 8 using an aqueous solution of ammonia. Relevant details are represented in *Scheme 1* and *Table I*.

(Take in Scheme 1)

(Take in Table I)

### **Latex formulation strategies**

#### *Using a different monomer system*

By changing the type and ratio of monomer VAM, VeoVa 10 and BuAc at a fixed ratio of anionic emulsifier SLS and non-ionic emulsifier NP30 ratio, the recipe for the synthesis is given in *Table I*.

### **Preparation of water-based flexographic inks**

Pigmented ink exists as a dispersion and the state of dispersion is dependent upon the formulation and the process of manufacture. The normal method of measurement is the grinding gauge consisting of a metal wedge graduated from 0 to 25 µm. Thus, the ink is drawn down the wedge with a blade until pigment particles begin to form scratches. This is then taken as the particle size (although more likely as an indication of the size of pigment particle aggregates). Care should be taken that the test is conducted prior to the addition of waxes etc. since these will interfere with the result. Other indications of the dispersion state are gloss, colour development and transparency and these are also monitored. Alterations in settings controlling the conditions on milling equipment will give rise to variations in quality of dispersion and careful monitoring will be needed to avoid batch variations. Chip-based inks are more consistent from batch-to-batch than with other methods of high dispersion. Chipping can, however, induce loss of flow due to the high dispersion state achieved. While processing plays a major part in producing the dispersion, there is a considerable influence and interdependence between the binder, pigment and solvent. All are equally important to the final result, particularly with respect to the dispersion stability. Finding the optimum conditions and formulation balance for maximising dispersion for a particular product can be time consuming, and involve numerous experiments. There is little doubt that bulk manufacture of single pigment bases, leading to fewer products milled, is to be preferred since in this way only a few products have to be studied. Stability of the dispersion is important, both with neat ink as supplied and diluted ink as used on the press. The adhesion and flexibility of water-based inks to impervious substrates is controlled by the selection of polymer emulsion. These are usually based on acrylic resins and there are a wide range of types available. The softer, low- $T_g$  (glass transition temperature) polymers normally give the better adhesion and flexibility properties when used on many film substrates, but these polymers have poor heat resistance. Typical water-based flexographic ink formulations would contain the following: 10% of VAM, VeoVa 10 and BuAc terpolymer of different types of polymer, 18.4% alkali soluble acrylic co-polymer, 51.94% water, 0.36% antifoam, 0.1% antibacterial, 2%

isopropyl alcohol, 3% polyethylene wax emulsion, 0.2% wetting agent and 14% pigment. Recipes of flexographic ink formulations containing the prepared nano-emulsion terpolymers are represented in *Table II*. Following stirring to achieve a good dispersion, the pH value should be 8-9, viscosity a 50-60 second measurement using Ford cup No. 4 at 25 °C, and grind should be 0-5 microns. The degree of dispersion was measured using a fineness of grind gauge. Also, water resistance and colour strength were measured.

(Take in Table II)

## **Characterisation**

### ***Transmission electron microscopy (TEM)***

The morphology of the copolymer particles was examined using transmission electron microscopy (TEM). In TEM, the dry sample was transferred into ultra-high vacuum and exposed to a high energy beam of electrons (100 keV). In an ideal case, a lateral resolution of around 1 nm is achievable. To perform TEM analysis, the latex was diluted with distilled water, with a drop of the diluted latex being placed on a carbon-coated grid and dried in a dissector. Then, 1-2 drops of a 0.8 wt.% aqueous solution of phosphor tungstic acid (PTA) was used to stain the particles. The shape and particle size distribution of the nanoparticles were determined using a JEOL-JEM-1011 transmission electron microscope.

### ***Gel permeation chromatography (GPC)***

The weight-average (M<sub>w</sub>) and number-average (M<sub>n</sub>) molecular weights were determined using an Agilent 1100 series gel permeation chromatography (GPC) system, equipped with a G1362A refractive index detector with 100-104-105 Å° ultra styragel columns. Polystyrene was used as a standard. THF was used as an eluent with a flow rate of 1 ml/min.

### ***Coagulum***

Coagulum of the polymer is generally done on a 100 g lot, and are a simple gravimetric determination of that percent retained on a 100 mesh. This can be put in a ring stand and the latex sample poured through quickly. Dilution with water will speed up the process for viscous latexes, provided the dilution doesn't cause coagulation. The screen is pre-weighted (dry). And the coagulum collected were determined according to ASTM D4828.

### ***Density***

A pycnometer, having a volume of 50 cm<sup>3</sup> is utilised to determine the density of the emulsions, at 25 °C. Thickness of polymer is more noteworthy than 1 g/cm like all the water-based latex. Exceptional hydrometers are likewise utilised for fast assurance of latex thickness. Thickness esteem is essential for the vehicle and shipment of the fabricated latex, it has less logical disadvantages.

### ***Thermo gravimetric analysis (TGA)***

TGA analysis was performed using a Shimadzu TGA-50 thermo gravimetric analyser (Columbia, EUA) using a nitrogen atmosphere and a heating rate of 10 °C/min over the temperature range between room temperature and 600 °C.

#### *Fourier transform infrared (FT-IR)*

The FT-IR analysis of the dried polymer samples was carried out using a JASCO FTIR 6100 in the range of 4000–400 cm<sup>-1</sup>.

#### *Viscosity*

The consistency of the flexographic inks was assessed by utilising a Ford viscosity cup number 4 at 25 °C by filling the cup with the fluid under test, and recording the time taken for the material to run through the standard openings.

#### *Degree of dispersion*

This test method describes the procedure for determining the fineness of grind of the printing inks, using a NPIRI grindometer. It evaluates the size of the largest particles in finished dispersion but not the average particle size, or the concentration of size. This test method is applicable to any dispersion that is fine enough to fall within the 0–25 µm range of the specified grind gauge. With a minor variation in procedure, it is applicable to both paste (non-volatile) and liquid (volatile) inks (ASTM D 1200).

#### *Colour density*

Inks formulated from the prepared terpolymer were applied onto white paper using an anilox applicator. The colour density of the printed sample was then measured using an ultra-scan pro spectrophotometer.

### **Results and discussion**

This work was expected to provide an ideal 50% emulsion for modern day application in water-based flexographic inks. Thus, a significant number of trials were undertaken in an attempt to create an ideal performance product from VAM, VeoVa 10 and BuAc terpolymer emulsion, having stable properties for a time-frame of 6 months. Also, with an aim to achieve a low coagulum of VAM, VeoVa 10 and BuAc terpolymer, the prepared polymers were investigated by testing for: solid content %, wet coagulum 100 mesh (g/l), particle size (nm), viscosity (cP), molecular weight, hardness, adhesion and pH. Characterisation of these systems was undertaken using TEM, TGA and FT-IR spectroscopy.

#### **Characteristics of the prepared emulsion terpolymers of VAM, VeoVa 10, BuAc, and the effect of SLS and NP30 surfactant system (Group IV)**

The physical, chemical and mechanical properties of the prepared VAM, VeoVa 10 and BuAc terpolymer containing SLS as anionic surfactant and NP30 as non-ionic surfactant (Group IV) were examined according to an international standard, as shown in Table III and represented

also in *Scheme 1*. Also, the pencil hardness test and the bending test of the film and adhesion to different substrates, were examined and recorded in *Table III*.

(Take in Table III)

#### ***Effect of SLS, SULFOPON 12G and NP30 surfactant system on solid content of Group IV***

The solid content of the prepared copolymers was determined gravimetrically. It was found that solid content depends mainly on the polymerisation rate and reaction conditions and less so on monomer composition. It is clear from the data that Group IV Sample G had the maximum solid content 50, while Group IV sample H lower than the Sample G. Also, we can conclude that as the hydrophobic monomer increased, the solid content decreased for all the groups. In addition, the values of the solid content slightly increased by altering the type of anionic surfactant sodium lauryl sulphate (SLS).

#### ***Effect of SLS, and NP30 surfactant system on the viscosity of Group IV***

Viscosity is the proportion of shear stress to shear stress. The viscosity of a latex at any given total solids content, decreases with increasing particle size and with increased broadening of the particle-size distribution. It is clear from the data that group IV sample H has a higher viscosity than group IV sample G as show in figure 3. Also, we can conclude that as the hydrophobic monomer increases, the viscosity also increases. The viscosity value also increases slightly by changing the type of anionic surfactant SLS. Low viscosity may reduce the film thickness of the flexographic inks and may decrease the spreading of the ink on the surface.

#### ***Effect of SLS, and NP30 surfactant system on the particle size of Group IV***

The particles must be small to allow a film to develop around the beads in the scattering stage. Diminished molecule measure allows more particles to be circulated at the limit, yielding a more stable emulsion. The size of emulsion particles is affected directly by the emulsification system, conditions of polymerization, and the relationship between the ter-monomers. It was observed that Group IV has the largest size of emulsion particles. Also, we can conclude from Figure 3 that as the hydrophobic monomer increases, the size of the particles decreases. Thus, the large particles allow for film development in a flexographic ink formulation.

#### ***Effect of SLS, NP30 surfactant system on molecular weight and molecular weight distribution Group IV***

As mentioned previously, molecular weight is an important factor affecting many polymer characteristics. All the molecular weights for the prepared samples are tabulated in *Table III*.

#### ***FTIR spectroscopy of the prepared terpolymer (Group IV)***

The FT-IR spectrum shown in **Figure 1**, of the Sample G and H Group IV illustrates the following groups: the carbonyl group C=O double bonds appears in the region of 1733.2 1731.1  $\text{cm}^{-1}$ , the band at 2965, 2972  $\text{cm}^{-1}$  is specific for aliphatic hydrocarbon of butyl acrylate and vinyl acetate, whereas the band at 3368, 3322  $\text{cm}^{-1}$  is due to – OH group and – NH<sub>2</sub> of acrylamide.

The FT-IR spectrum of latex shows that VAM, VeoVa 10 and BuAc participated in the polymerisation reaction, and that terpolymerisation latex was prepared.

(Take in Figure 1)

#### ***Thermo gravimetric analysis (TGA)***

The TGA curves of the VAM, VeoVa 10, BuAc nano-emulsion terpolymer (presented in Figure 2) of Sample G, indicated that the initial decomposition temperature starts at 200 °C, with final decomposition starting at 412 °C. The sample is shown to have fully decomposed at a temperature of 510.1 °C. The result is a total mass loss of 77.50% weight, while the percentage of residue is 6.3% weight. The TGA thermogram of Sample H as in *Figure 5* shows that the initial decomposition temperature is 200 °C, while it starts to complete final decomposition at 414 °C and is completely decomposed at a temperature of 512.1 °C. The result is a total mass loss of 78.50% weight, while the percentage of residue is 5.4% weight.

(Take in Figure 2)

#### ***Transmission electron microscopy (TEM) of the prepared terpolymers G and H (Group IV)***

Transmission electron microscopy electron micrographs show that the diameter of most particles of Samples G and H were between 150 and 200nm (*as shown in Figure 3*) with a narrow size distribution. These were prepared from VAM, VeoVa 10, and BuAc terpolymer in the presence of acrylic acid and acrylamide monomer. It is clear from the micrographs that the particles are spherical in shape without any obvious deformation.

(Take in Figure 3)

#### ***Storage stability test***

As a multifunctional additive, hydrophobic alkali swellable emulsion (HASE) makes it possible to reduce costs and still obtain performance equal to or better than that of similar ink formulations containing thickener. In order to check the long-term stability of the ink and its dependence on nano-emulsion binder (Abd El-Wahab, 2018), it is recommended to store the ink at elevated temperatures (50-60 °C) for two weeks and to check viscosity and colour strength afterwards. Insufficient storage stability might lead to flocculation. This is the general term for weakly interaction between associative thickener and binder because the main ingredient for anti-settling in ink formula is acrylic associative thickener as shown in Table III and the latex has large particle size. Settlement leads to loss of gloss, loss of colour strength and settling tendency.

Characterisation of the water-based flexographic ink :

#### **Viscosity, water resistance and Colour density of the prepared flexographic ink based on the nano-copolymers as a binder**

Samples of the prepared nano- terpolymers were incorporated into emulsion water-based ink formulations as a binder and evaluated. The samples were compared with a commercial trademark reference co-polymer (Joncryl). The results obtained for water resistance, Colour

density and viscosity, based on the nano- terpolymers as a binder, showed improved values when compared with the commercial reference sample (Joncryl). The data are shown in *Tables IV*. Flexographic water-based inks are used for printing on paper, carvings and duplexes and are used in the manufacture of cans and carton boxes. Also, there are thermoplastic inks used for printing on plastics and textiles. Water-resistance in the printed product was assessed by using VAM, VeoVa 10 and BuAc terpolymer emulsion. The terpolymer emulsions were incorporated into a standard formulation for water-based flexographic inks and compared with a co-polymer emulsion used in industry (Joncryl) as previously illustrated in *Table III*. The prepared water-based flexographic inks were tested for viscosity, pH, fineness of grind and water resistance, as shown in *Table IV*. Table VI summarises the results obtained for the water-based flexographic inks using Group IV Samples G, H, and Joncryl 90 in standard ink formulations.

(Take in Table IV)

#### **Viscosity, water resistance and colour density of the prepared flexographic ink based on the nano-terpolymers as a binder**

*Table IV* summarises the results obtained from the water-based flexographic inks using Group IV and Joncryl 90 in standard formulations to study the difference between Group IV and the trademark emulsion polymer.

##### ***Viscosity***

The high solubility of VAM in water leads to difficulties during copolymerisation with more hydrophobic monomers, since the relative concentrations of the copolymerising monomers in the polymer and water phases are significantly different. This makes the viscosity of the prepared terpolymers in Group IV lower in comparison to the trademark co-polymer (Joncryl 90).

##### ***Water resistance***

Due to the high solubility of vinyl acetate monomer in water, the water resistances of the prepared terpolymers did not achieve satisfactory results. In addition, BuAc in terpolymer. VAM, VeoVa 10 and BuAc terpolymer shows less capacity of hydrophobicity than the trademark co-polymer (Joncryl 90) of which the colour of the printed paper following the water immersion test fades. The water resistance photo-macrograph of water-based flexographic ink samples using Samples G, H of Group IV, are shown in *Figure 4*.

(Take in Figure 4)

##### ***Colour density***

Print quality is expressed by image sharpness, colour, tone, gloss, print density, legibility and the uniformity of these properties (Hussain, 2010). The specular gloss relies on the surface structure and porosity of the substrate, while the print density is evidence of a thicker ink layer. This is a consequence of the wider coating network and the stronger bonding between the base paper and the ink (Gigac, 2011).

With respect to gloss and density, the size and shape of the pigment particles have a real impact on both the coating and the printing processes. The gloss of a coated sheet is reliant on the coating covering the fibres and on the roughness of that coating. The latter has a unified two prime component that produces the surface topography and consequently its gloss. Firstly, the pigment particles contribute to the small-scale micro-roughness due to their size and shape, and the mode by which they pack together on the surface of the paper. Secondly, the base paper fibres just beneath the coating, impact the surface roughness, particularly at low coat weights since a low amount of coating does not entirely match fibre size and shape.

Using nano-emulsion terpolymer as a binder for the flexographic ink resulted in an average gloss reading of 37-42, while its print density was 1.3 and 2.0. Print gloss and print density were directly correlated. An explanation could be that low print gloss is evidence of a rough print surface, which indicates that when print density is low, poor quality image and colour reproduction is obtained (Sonmez, 2011). Also, based on the tabulated results, the type of surfactant can play an important role on the final properties. It can be observed that changing the type of anionic surfactant SLS, leads to a slight increase in colour strength, together with density. All the mechanical and physical characteristics obtained of water base flexographic inks using Group IV based on VAM, VeoVa 10 and BuAc terpolymer Group IV were tabulated in *Table IV*.

## Conclusions

It is clear that Group I samples have the maximum solid content, while Group III samples have the minimum solid content. It can be concluded that as the hydrophobic monomer increased, the viscosity increased. The solid contents of the prepared terpolymers were determined gravimetrically. It was found that the solid content mainly depended on the polymerisation reaction conditions. The viscosity of a latex at any given total solids content decreased with increasing particle size and with increased breadth of the particle-size distribution. It was observed that the average gloss by using nano-emulsion terpolymer as a binder for flexographic ink was 37-42 while its print density was 1.3 and 2.0. It was also observed that print gloss and print density were directly correlated, and that particle size specifically affected the physical solidness of emulsions.

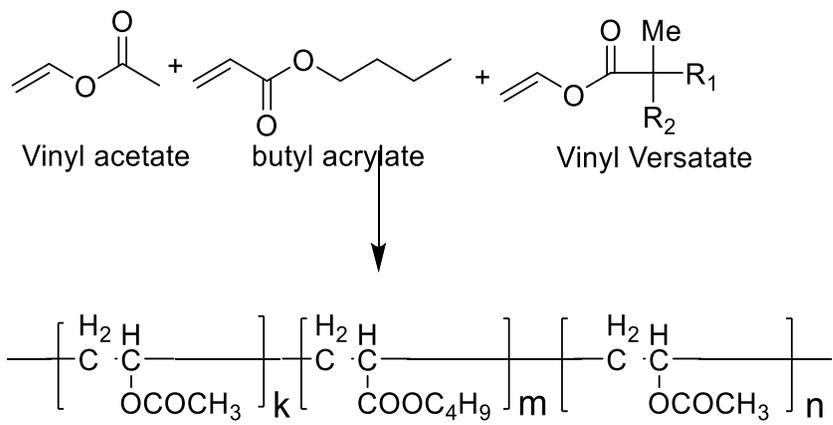
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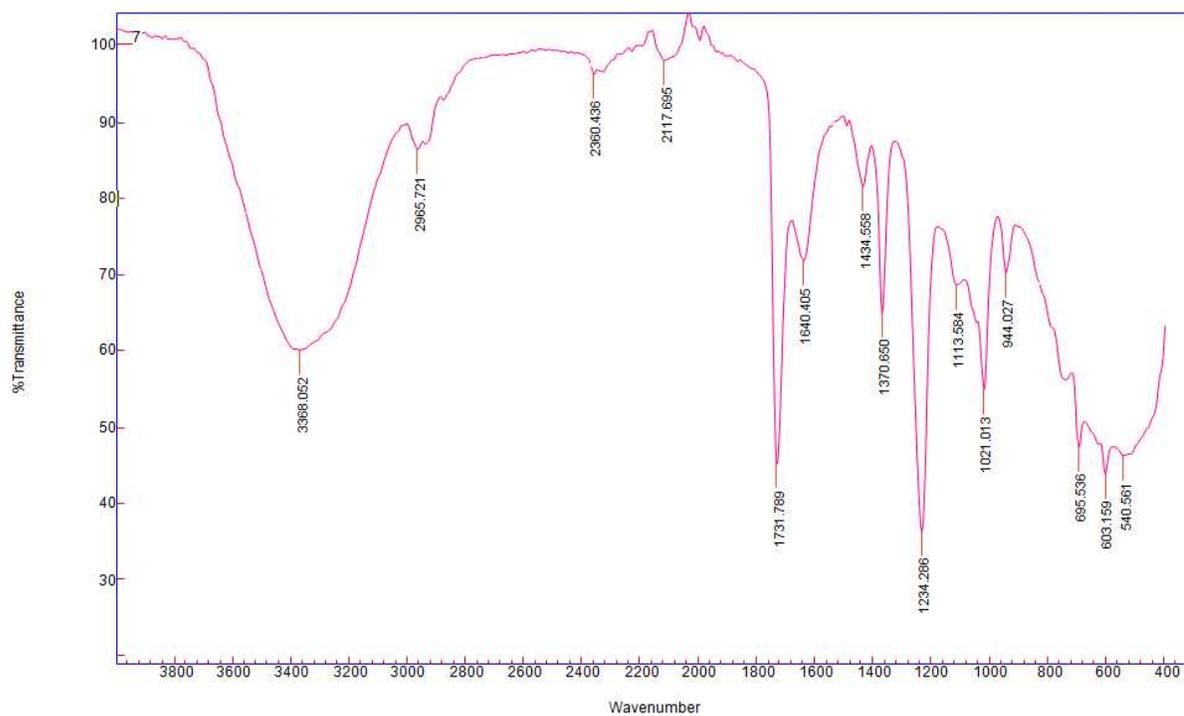
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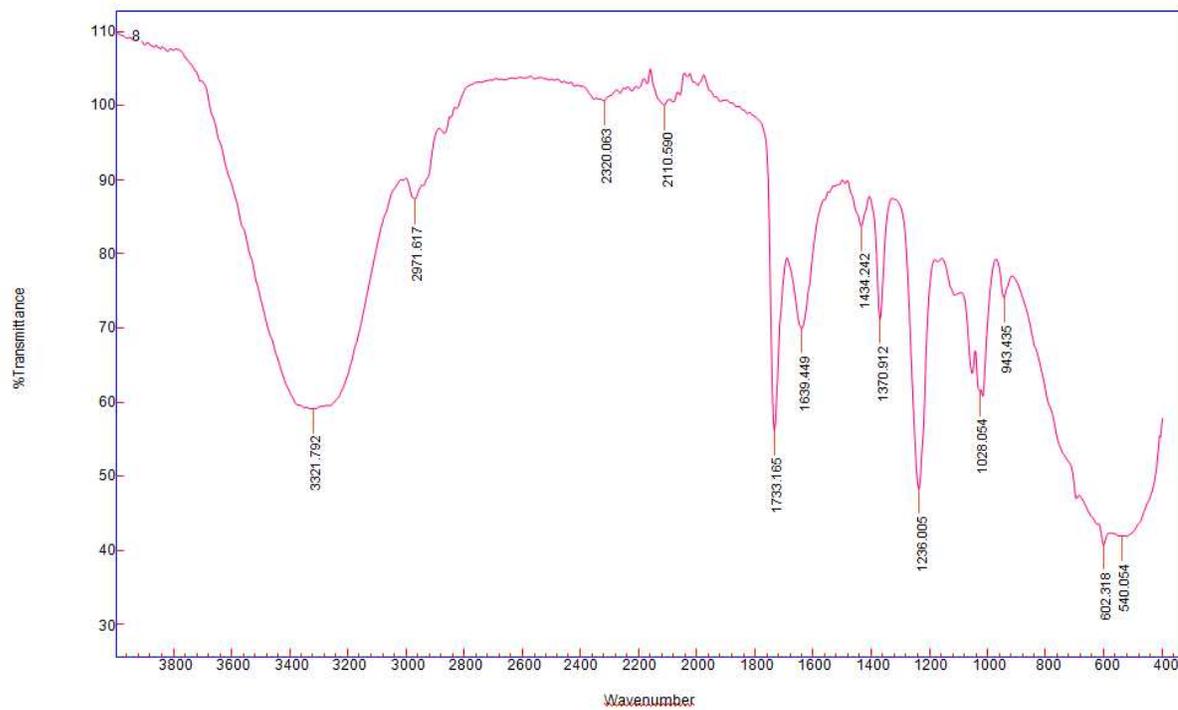


Scheme (1): Chemical reaction between VAM, VeoVa 10 and BuAc terpolymer

### Sample G

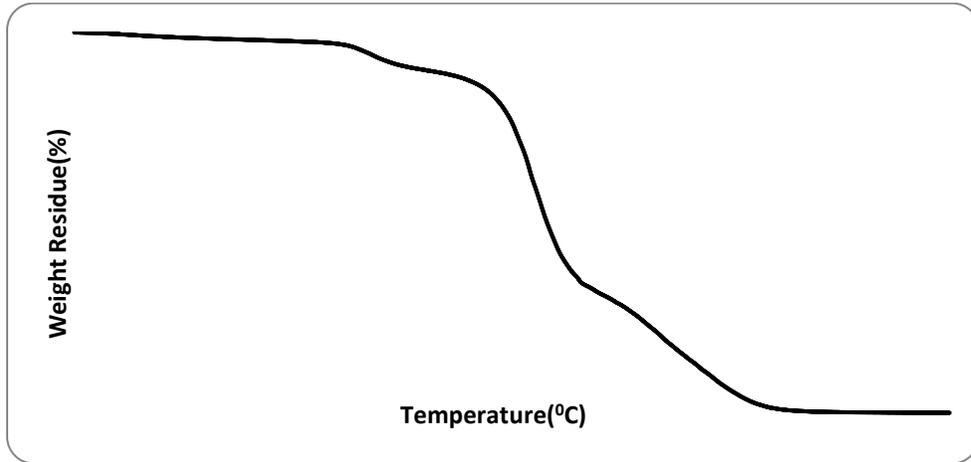


### Sample H

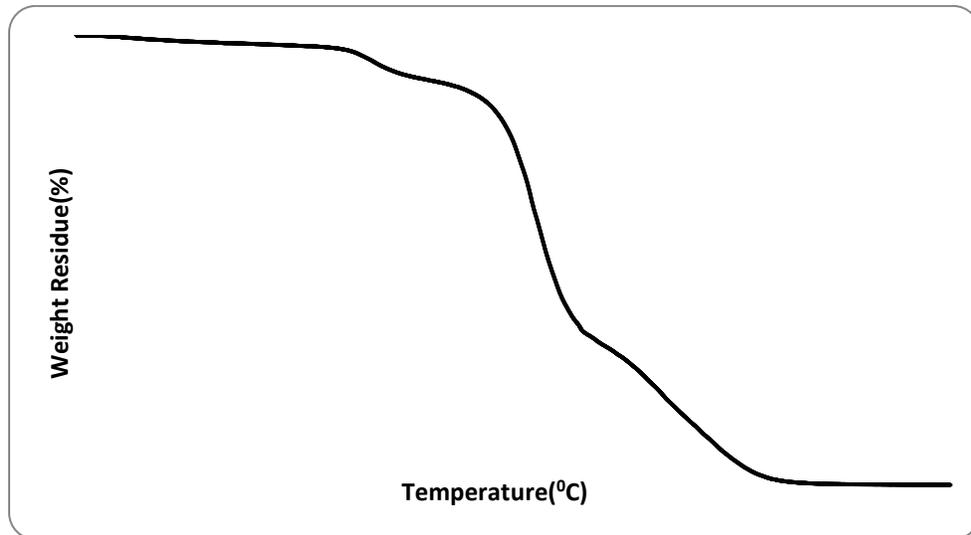


**Figure 1** FT-IR spectra of VAM, VeoVa 10 , BuAc and acrylic acid terpolymer Group IV sample H

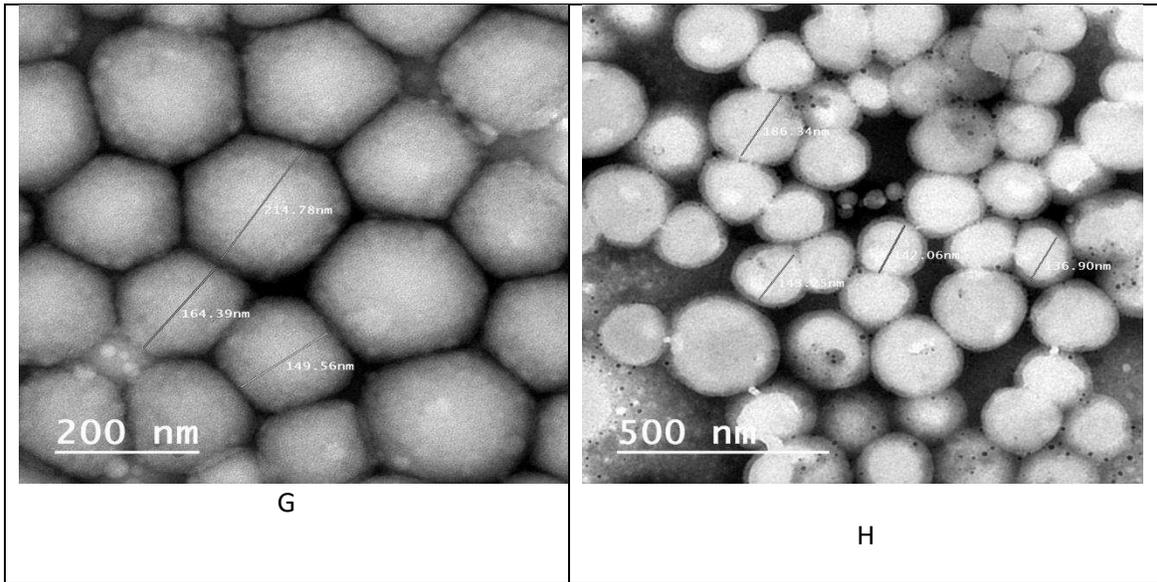
Sample G



Sample H



**Figure 2** TGA curve for sample G and sample H (Weight loss versus temperature)



**Figure 3** Transmission electron micrographs of the prepared emulsion terpolymer Sample G, Group IV (avg. 120nm) and sample H Group IV (avg. 130nm).



Blank



Sample G



Sample H

**Figure 4** Water resistance photo-macrograph of water-based flexographic ink samples using Sample G Group H, Group IV comparing with the blanket sample for trade mark co-polymer (Joncryl 90).

**Table I** Recipe for different ratios of VAM, VeoVa 10 and BuAc and butyl acrylate (BuAc) terpolymer containing of SLS as anionic surfactant, NP30 as non-ionic surfactant

Component*	Group (IV)	
	G	H
Vinyl acetate	42.5	42.5
Butyl acrylate	3.75	5
Vinyl Versatate (VeoVa 10)	3.75	2.5
Sodium lauryl sulphate (SLS)	2.2	2.2
NP30	0.4	0.4
Distilled water	48	48

\*All ingredients weighted in grams.

The above recipe contains potassium persulphate as free radical initiator (0.2 g), acrylamide monomer (0.1) and Acrylic Acid (2 g). Temp 80°C, pH 8.5.

**Table II** Recipes of Flexographic Ink formulations containing the prepared nano-emulsion co and terpolymers

Ingredients*	Group (IV)	
	G	H
VAM/VeoVa 10/BuAcTerpolymer	10	10
Pigment red 49:1	4.8	4.8
Pigment red 81	0.2	0.2
Pigment red 2	9	9
Alkali soluble acrylic co- polymer	18.4	18.4
Antifoam	0.36	0.36
Antibacteria	0.1	0.1
Wetting agent	0.2	0.2
PE wax emulsion	3	3
Isopropyl alcohol	2	2
Water	51.94	51.94

\*All ingredients weighted in grams.

**Table III** Characterisation of the prepared VAM, VeoVa 10 and BuAc nanoemulsion terpolymer [group (IV)]

Properties	Standard	Group (IV)	
	ASTM	G	H
pH		7.5	7.7
Solid Content (%)	D2369	50	49.3
Particle size (nm)	TEM	150	160
Brookfield Viscosity RVT #50 rpm, (cps)	D 2196	2000	2400
Molecular weight	$M_n \cdot 10^4$ (g/mole)	5.5	4.3
	$M_w \cdot 10^5$ (g/mole )	4.13	3.97

**Table IV** Mechanical and physical characteristics obtained of water base flexo inks using group (IV) based on VAM, VeoVa 10 and BuAc Terpolymer [group IV]

	standard formulation	Group (IV)	
		G	H
Viscosity (Sec) Ford Cup No. 4 at 25°C	60	45	48
PH	9	9	9
Water Resistance	Excellent	Very Bad	Bad
Grinding	5	5	5
Gloss	42	34	37
Colour Strength (density)	2	1.3	1.5