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Research Article

SYNTHESIS OF SOME NON-IONIC-DISPERSING AGENTS AND ITS APPLICATIONS AS PIGMENT DISPERSANTS FOR PRINTING INKS

Yasser Assem[1*], AAF. Wasfy[1] and M. Abdulazeem Sayed[2]

[1]Polymer and Pigments Department, National Research Center, Giza, Egypt
[2]Chemistry Department, Faculty of Science, Benha University, Benha, Egypt.

ABSTRACT

The esterification of different saturated fatty acids with polyethylene glycol of molecular weight 600 Dalton were synthesized and applied as non-ionic organic pigment wetting and dispersing agents in manufacturing of liquid printing inks as economic wetting and dispersing additives against the other dispersants based on ethoxylated polyether types which are more expensive and its synthesis are more complicated. Meanwhile, it has a hazardous effect on labors health as it is not eco-friendly due to the highly emission of ethylene oxide monomers during its production.

FTIR, H^1NMR and GPC were studied to confirm the synthesized dispersants, in addition to its gloss, transparency and viscosity to study the efficiency of these dispersants in printing inks with diverse organic pigments.

Keywords: Non-ionic dispersing agents, printing inks, polyethylene glycol-fatty acid dispersant.

INTRODUCTION

As functional and performance requirements from the industries that deal in paints, printing inks, cosmetics and other pigment dispersion substances become increasingly more intricate and diverse, dispersion of pigment continues to be one of major technical challenges. The smaller size of the pigment particle, the more fully the capabilities and properties inherent in the particle will be exerted and better results can be expected. In many cases, however, the vehicle alone is not enough to obtain required dispersibility and thus wetting agents and dispersants become necessary. Wetting agents and dispersants, even a small amount of which can produce effects, are very effective and offer an easy way to make good pigment dispersion substances and products.

The present invention relates to the synthesis of some non-ionic organic pigment dispersants based on different fatty acids with polyethylene glycol of molecular weight 600 dalton via esterification reaction which represent a simple technique, cost benefit, safe and ecofriendly industry against ethoxylation products.

The condensation products of fatty acids with polyethylene glycols comprise monoesters and Esterification is a state of equilibrium where water must be removed as soon as it is formed. This can be done by carrying out the process at temperatures above 100°C and/or in the presence of a proper homogenous catalyst or an Azeotrop in an isotropic distillation.

Preparation and emulsifying properties of Polyethylene Glycol (1500) Diesters of fatty acids Wase discussed by D.N Bhattacharyya[1]. Preparation and Surface-Active Properties of Polyoxyethylene glycol (600) Monoesters of Fatty Acids was achieved[2]. Polyoxyethyleneglycol (PEG) monoesters of fatty acids, being low foamers and good emulsifiers, find extensive use in textile industry and pesticide formulations and also in cosmetic preparations[3]. PEG fatty acid esters are prepared by either ethoxylation[4,5] or esterification[6]. The latter process is safer and more easily controllable as desired. Even here, considerable proportions of diesters are formed unless a large excess of glycol is employed[7]. Pure monoester can be readily obtained by forming a borate with glycol and esterifying with a fatty acid[8]. This route has been applied earlier for the preparation of a variety of monoesters of ethylene glycol as intermediates for pure mixed diesters[9].

We intend to esterify lauric, myristic, palmitic and stearic acids with polyethylene glycol of molecular weight 600 dalton as non-ionic pigment dispersants for gravure printing inks

industry, as we'll prepare a series of pigment dispersants which are efficient, cheaper and eco-friendly than commercial grades like Solsperse® 20000 (from Lubrizol Company, England) to be serve the domestic market in Egypt as local supply.

2. EXPERMINTAL

2.1. MATERIALS

Polyethylene glycol of molecular weight 600 was supplied from CarlRoth, (Germany), Lauric, myristic, palmatic and stearic acid were supplied from Aldrich Chemical Company (USA), Titanium butoxide catalyst was supplied from Drof Katel company (India), Pigment yellow C.I 13, Pigment red C.I 57:1 were supplied from Hangzhou pigment Company (China), Pigment blue C.I 15:4 was supplied from Ramadev Company (India), carbon black was supplied from Spring Green (China)., Nitrocellulose 18-25 BN was supplied from Nitro Quimica Company (Brazil), Solsperse® 20000 was supplied from Lubrizol Company (England), Ketonic resin was supplied from DR Coat (India), Acetyl tributyl citrate was supplied from Egy Polymers Company (Egypt), Ethylacetate, Ethanol and Methoxy propanol supplied from Sasol (South Africa), Glass beads mills 0.3 and BOPP film were supplied from PAN Egypt Company (Egypt).

All chemicals and materials were used without further purification.

2.2. DISPERSING AGENTS PREPARATION

2.2.1. GENERAL PROCEDURE FOR SYNTHESIS OF DISPERSANTS

The reaction was carried out in a 500ml round glass flask equipped with Dean and Stark apparatus with porcelain balls (2ml in diameter) as stirrer. Heating was conducted in a thermostatic oil bath. 0.2 mole of dried fatty acid to 0.22 PEG was melted at 70°C and thoroughly mixed with a specific amount of titanium (IV) n-butoxide as in table 1. Then, Dean and Stark apparatus was fitted onto the flask in an oil bath. The temperature raised from 70°C to 180°C, where the reaction held for 12 hrs then the flask was taken out of the bat and cooled at room temperature then samples were discharged for purification, analysis and application.

2.2.2. PRODUCT PURIFICATION

The mixture of esters was separated from unreacted fatty acid and PEG by dissolving the products in ethyl acetate at a liquid / product ratio of 10:1 at 35 ± 1°C, and transferred to a separating funnel (about 3 times the volume of the ethyl acetate solution).

5 successive washings were given to the ester solution, each with an equivolume amount of the aqueous solution containing NaCl (30 weight percent) and NaOH (2 weight percent to remove the fatty acid and catalyst), followed by 5 successive washings, each of equivolume amount, to remove salinity and remnant alkalinity. The ethyl acetate layer was then evaporated in a rotavapour at 80°C in a vacuum until dryness to get the purified esters[10].

2.3. CHARACTERIZATION OF PREPARED DISPERSANTS

Nuclear magnetic resonance (1H NMR) spectra were recorded on Jeol ECA-500 run at 500 MHZ. The synthesized samples were dissolved in $CDCl_3$, and tetramethylsilane was used as the reference standard.

Infrared spectroscopy (FTIR) the FTIR spectra of polymers were recorded by JASCO FTIR 6100 in the range of 4000–400 cm^{-1} using KBr pellets.

2.3.1 (^{1}H NMR) OF PREPARED DISPERSANT

Figure (2-3) shows ^{1}HNMR of the prepared dispersant. The protons of the fatty acid segments of the dispersant could be assigned as follow, four protons of Fatty acid moiety (a Fig 2) at ppm 0.82, four protons of PEG (b Fig 2) at ppm 2.4 and four terminal protons of polyethylene glycol (e, f Fig 2) at ppm 3.6 and 4.3.

By the same way, the structure of all block copolymers were elucidated and represented in Figure 3

2.3.2 (FTIR) OF PREPARED DISPERSANTS

The FTIR of the prepared dispersants with PEG have Molecular weight. 600 are shown in figure 3. The characteristic bands could be assigned as follow; C=O stretching band of the ester group occurs at 1737 cm^{-1}, C-O stretching band occurs at 1170 cm^{-1}, C-H stretching occurs at 28801cm^{-1}, 2956 cm^{-1} (symmetrical and asymmetrical respectively), CH_2 bending occurs at 1463 cm^{-1} and OH stretching band at 3458 cm^{-1}. The IR charts for dispersants with different saturated fatty acids shown in figure 4. There is no difference in the peak assignment of the all dispersants.

2.4. EVALUATION OF THE SYNTHESIZED OF PRODUCTS AS PIGMENT DISPERSANTS

PRINTING INKS PREPARATION

The synthesized polymeric dispersants were applied in gravure printing inks formulations. The printing inks formula must have dispersant to overcome the pigment particles aggregation

and/or agglomeration to achieve the desired properties such as, gloss, color strength, transparency and viscosity. All synthesized dispersants were used in below formulations in table 2 with using diverse organic pigments such yellow C.I 13, Red C.I 57:1, Blue C.I 15:4 and Carbon black C.I 7 to evaluate its efficiency against Solsperse® 20000 and another blank sample. The dispersion process was applied with glass beads of 1mm diameter by using Red-Devil shaker for 60 minutes.

DRY FILM GLOSS MEASURMENT (ASTM D523)

The gloss degree was measured by a glossmeter of type Minigloss model of Sheen Instruments company from United Kingdom, with an measuring geometry 60 Degrees, resolution 0.1 gloss unit and accuracy ±1 .0 gloss unit (against reference standard).

SPECTRODENSITOMETER (ASTM D7305-08)

The Color hue, color strength and transparency were measured on a SpectroDensitometer of type X-rite 504 model of X-rite Company from United States, with an measuring geometry 45°/0°, Spot Size at Sample 3.4mm (.13in) standard and Measurement Range 0.00D–2.5D; 0–160%R with Measurement Time Approx. 1.4 seconds, approx..9 seconds for consecutive measurements in Speed Read mode and Repeatability ±0.005D.

VISCOSITY MEASURMENT (ASTM D1200)

The viscosity was measured on a cup viscometer of type ford cup#4 model of BYK-Gardner GmbH from Germany. It's has Efflux Time 20 - 105 and Orifice Diameter 0.16 in.

DRAWDOWN AND FILM PREPARATION

The drawdowns of prepared inks were applied at delivery viscosity on corona treated transparent BOPP film with using rubber bed and wire hand coater No. 1 (6 microns).

2.4.1 GLOSS MEASURMENT

The Gloss is the attribute of surfaces that causes them to have shiny or lustrous, metallic or matte appearances. The gloss values of printed films are very important data to explain the performance of non-ionic organic pigment dispersants synthesized because it's reflect the mechanism action of dispersion of aggregates and agglomerates of pigments particles.

In general, gloss of all pigmented systems, are affected to a greater or lesser extent by the size and distribution of the pigment particles in the dispersion. Generally, surface-treated pigments with dispersants are more easily dispersible, produce more stable dispersions in fluid media with improved gloss to the printed films, when compared with untreated pigments.

The gloss of printed film with gravure ink made by synthesized dispersants were evaluated and recorded in table 3.

2.4.1.1 GRAVURE INK OF PIGMENT YELLOW C.I 13

Inks prepared from all synthesized organic dispersants showed better gloss than inks prepared without using organic dispersants (Blank sample) as in Figure 5. The best gloss result of all synthesized organic dispersants was PEG600-M against Solsperse® 20000.

We noted that organic dispersants of Lauric and myristic acids give better results with pigment yellow C.I 13 than products of Palmitic and Stearic acids which may be attributed to the high polar surface of pigment yellow C.I 13.

2.4.1.2 GRAVURE INK OF PIGMENT RED C.I 57:1

Inks prepared from all synthesized organic dispersants showed better gloss than Solsperse® 20000. As in Figure 6. The best gloss result of all synthesized organic dispersants was by using PEG600-L which may indicates that dispersants of short chains of fatty acids are more suitable dispersants according to the chemical structure of pigment red C.I 57:1.

2.4.1.3 GRAVURE INK OF PIGMENT BLUE C.I 15:4

The synthesized organic dispersant of PEG600-M showed better gloss than Solsperse® 20000 and other dispersants based on Lauric, Palmitic & Stearic acids which may indicate that pigment blue C.I 15:4 was more suitable and efficient with dispersants of medium chain length from Lauric to Stearic acids as shown in Figure 7.

2.4.1.4 GRAVURE INK OF PIGMENT BLACK C.I 7

All synthesized dispersants were not efficient to disperse carbon black pigment as shown in Figure 8 because, these series of surface active organic dispersants are more efficient for polar organic pigments than carbon black surface which is considered as non-polar surface.

2.4.2. TRANAPARENCY MEASURMENT

It is usually determined by applying the pigmented system to a black back-ground

whose darkness is retained or reduced according to the transparency of the layer. Scattering increases the opacity of a layer. While the light transmitted increases by more transparent pigments. The transparency values indicate the dispersion quality and related to choice of dispersant selection.
The transparency data of prepared pigmented ink were recorded as in table 4.

2.4.2.1. GRAVURE INK OF PIGMENT YELLOW C.I 13
PEG600-M was the best dispersant when compared with blank and the other samples as in Figure 9. Actually, dispersants of short chains of fatty acids are more suitable for high polar surface pigments like pigment yellow C.I 13.

2.4.2.2. GRAVURE INK OF PIGMENT RED C.I 57:1
PEG600-L, PEG600-M and PEG600-P showed the best results against blank and the other samples. PEG600-S showed lower efficiency against all other synthesized samples but still better than Solsperse® 20000 as shown in Figure 10, which may be attributed to the high polarity of the pigment surface.

2.4.2.3. GRAVURE INK OF PIGMENT BLUE C.I 15:4
PEG600-M & PEG600-L showed the best results concerning optical transparency than Solsperse® 20000 & blank samples as in Figure 11, due to its medium fatty acids chain length which are more suitable with medium surface polarity of pigment blue 15:4.

2.4.3. VISCOSITY MEASURMENT
Viscosity, the resistance to flow, is the most important rheological characteristic of liquids and therefore of coatings and inks. Even more significant is the way in which viscosity changes during coating and printing. Newtonian fluids, like solvents, have an absolute viscosity that is unaltered by the application of mechanical shear. However, virtually all coatings show a significant change in viscosity [(11)]. The dispersants play important role to achieve low viscosity of dispersion medium during grinding stage and allow the formulator to make high pigment volume concentration without thixotropic phenomena which lead to save process, time and cost. The viscosity values of prepared pigmented ink were recorded as in table 5.

2.4.3.1. GRAVURE INK OF PIGMENT YELLOW C.I 13
All synthesized dispersants showed lower viscosities than Solsperse® 20000 as in Figure 12.
PEG600-P showed the lowest viscosity, which indicates its high efficiency as a dispersing agent for yellow pigment C.I 13.

2.4.3.2. GRAVURE INK OF PIGMENT RED C.I 57:1
PEG600-S showed the lowest viscosity which indicates its high efficiency as a dispersing agent for pigment red C.I 57:1 meanwhile, PEG600-L, PEG600-M & PEG600-P are still better than Solsperse® 20000 as shown in Figure 13.

2.4.3.3. GRAVURE INK OF PIGMENT BLUE C.I 15:4
PEG600-L has a comparable viscosity against Solsperse® 20000 but the other synthesized dispersants showed higher viscosities as shown in Figure 14.

2.4.3.4. GRAVURE INK OF PIGMENT BLACK C.I 15:4
For Carbon black C.I 7, no change in ink viscosities observed when synthesized dispersants were used against Solsperse® 20000 except for blank sample & PEG-600S which showed the highest inks viscosities as shown in Figure 15.

3. CONCLUSION
Esterification process was used in synthesis of series of non-ionic organic pigment dispersants including PEG600L, PEG600-M, PEG600-P & PEG600-S with different chain lengths of fatty acids to overcome disadvantages of ethoxylation process. The structures of the synthesized dispersants were confirmed by FTIR & ^{1}HNMR.
Gloss, transparency and viscosity of prepared gravure inks were measured and their performances were investigated for different organic pigments against Solsperse® 20000. Most of synthesized dispersants showed excellent gloss, transparency and viscosity which reflect the high efficiencies of these dispersants as new non-ionic dispersants for different organic pigments in printing inks industry.

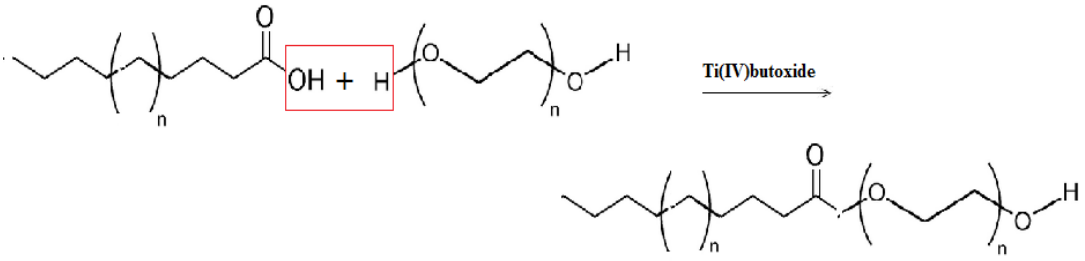

Fig. 1: Synthesis of fatty acid with polyethylene glycol in presence of titanium butoxide As homogenous catalyst

Table 1: Polyethylene glycol ratio to fatty acids in presence of titanium (IV) butoxide catalyst

No	Dispersant symbol	Hydrophilic part	Hydrophobic part	PEG weight (gm)	Fatty acid weight (gm)	Catalyst weight (gm)
1	PEG600-L	PEG 600	Lauric	132	40.00	0.040
2	PEG600-M	PEG 600	Myristic	132	45.60	0.044
3	PEG600-P	PEG 600	Palmitic	132	51.20	0.050
4	PEG600-S	PEG 600	Stearic	132	56.80	0.056

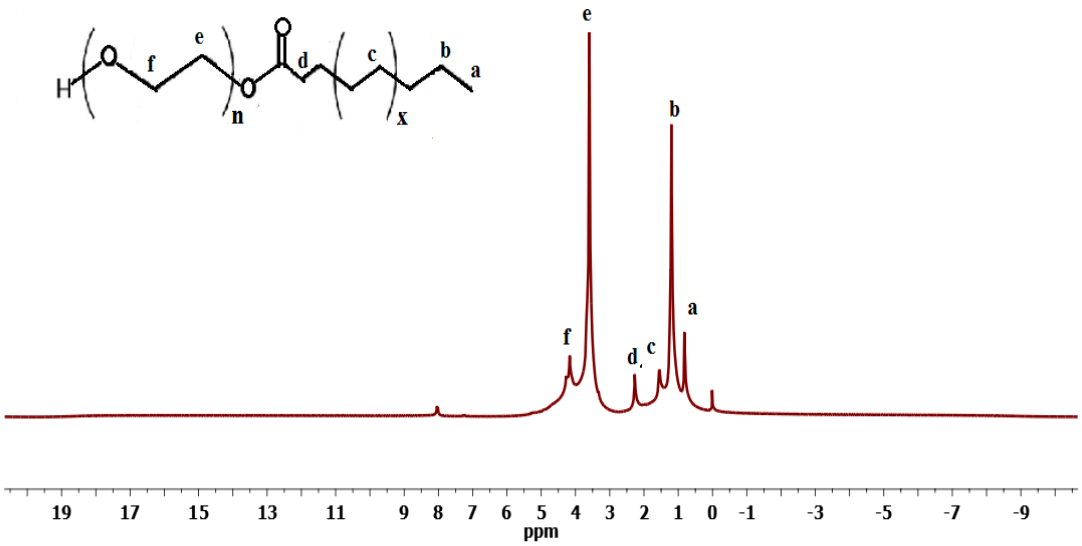

Fig. 2: Show ^{1}HNMR of PEG600-L.

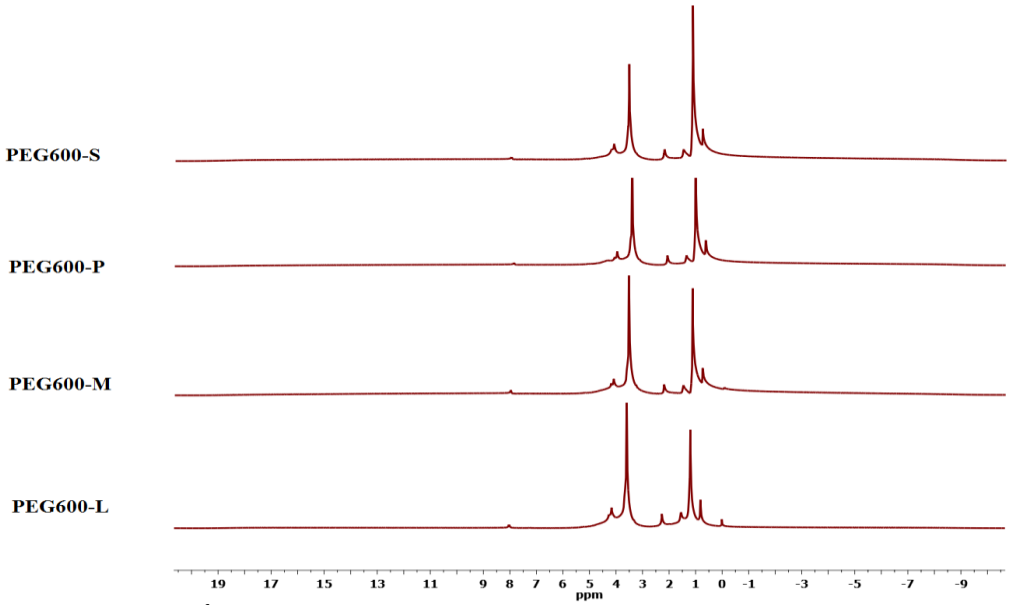

Fig. 3: ^{1}HNMR of PEG600-L - PEG600-M - PEG600-P - PEG600-S

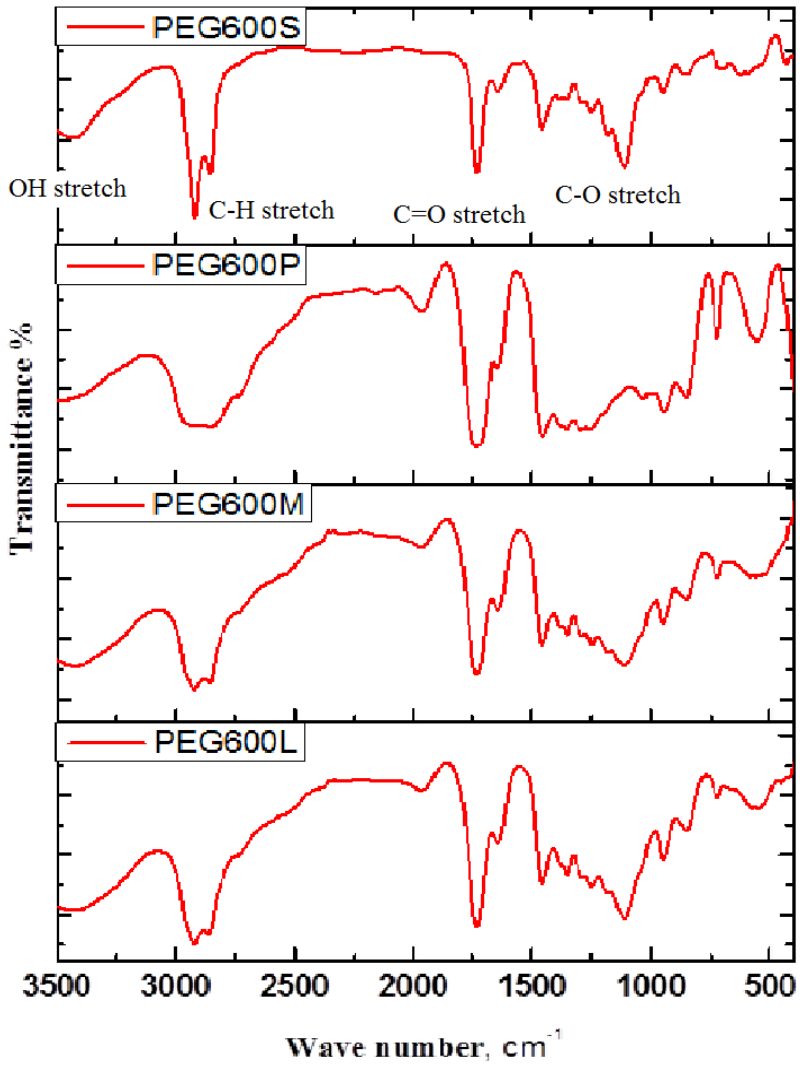

Fig. 4: Shows IR for all prepared dispersants

Table 2: Liquid printing inks formulations prepared by different dispersants *All synthesized dispersants (PEG600-L – PEG600 M – PEG600-P – PEG600-S), blank sample and Solsperse® 20000 were prepared with diverse types of pigments

Material	Cyan	Yellow	Magenta	Black
Pigment Cyan C.I 15:4	13	---	---	---
Pigment Yellow C.I 13	---	10	---	---
Pigment Magenta C.I 57:1	---	---	12	---
Pigment Black C.I 7	---	---	---	12
Dispersing agent*	2	1	1	3
Nitrocellulose 1/8 S	19	16	18	18
Ketonic resin	3	3	3	3
Acetyl tributyl citrate	4	4	4	4
Ethanol	15	34	15	15
Ethyl acetate	44	32	47	45

Table 3: Gloss of printed films with different pigmented inks by using synthesized dispersants against commercial and blank samples

No.	Dispersant	Yellow	Magenta	Cyan	Black
1	Solsperse® 20000	66	54	41	60
2	Blank	42	60	52	35
3	PEG600-L	65	80	48	38
4	PEG600-M	70	78	72	45
5	PEG600-P	42	79	65	40
6	PEG600-S	58	65	50	32

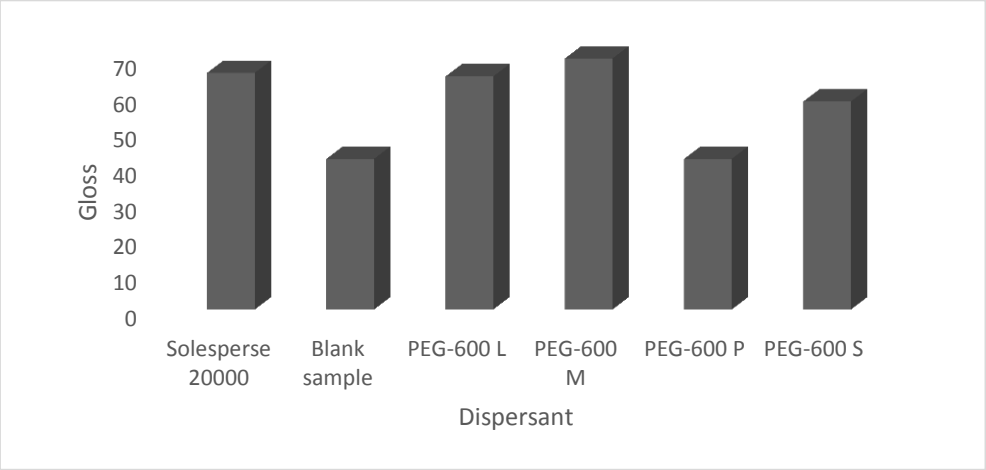

Fig. 5: Gloss of yellow gravure ink were prepared by synthesized dispersants

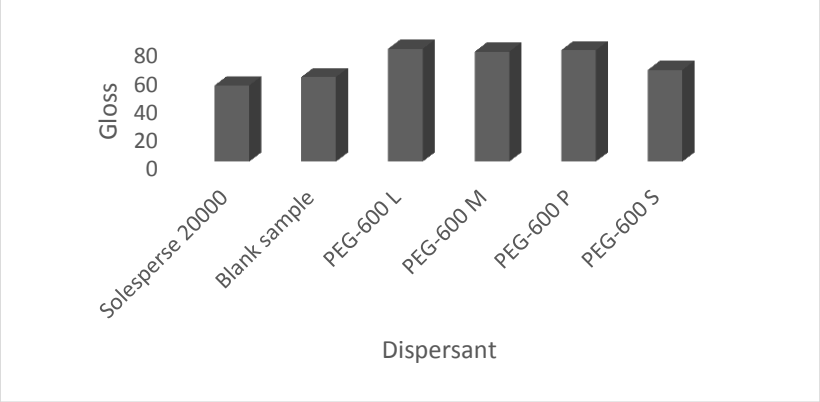

Fig. 6: Gloss of Red gravure ink were prepared by synthesized dispersants

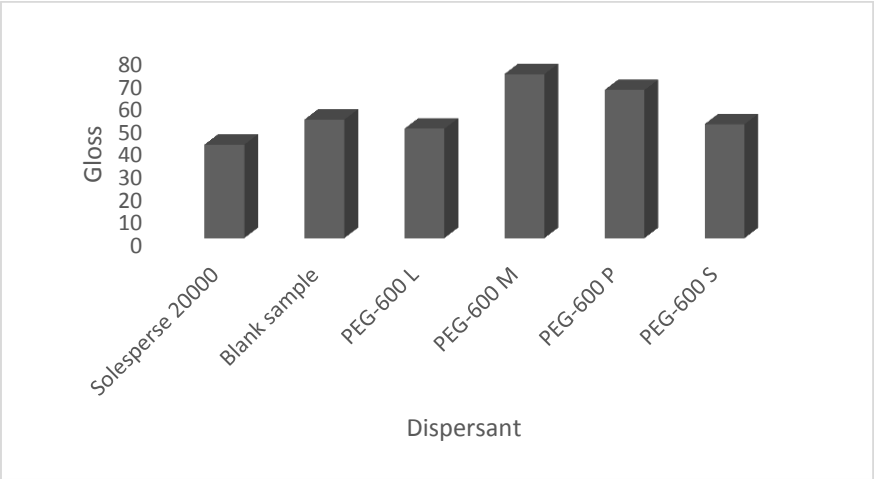

Fig. 7: Gloss of Blue gravure ink were prepared by synthesized dispersants.

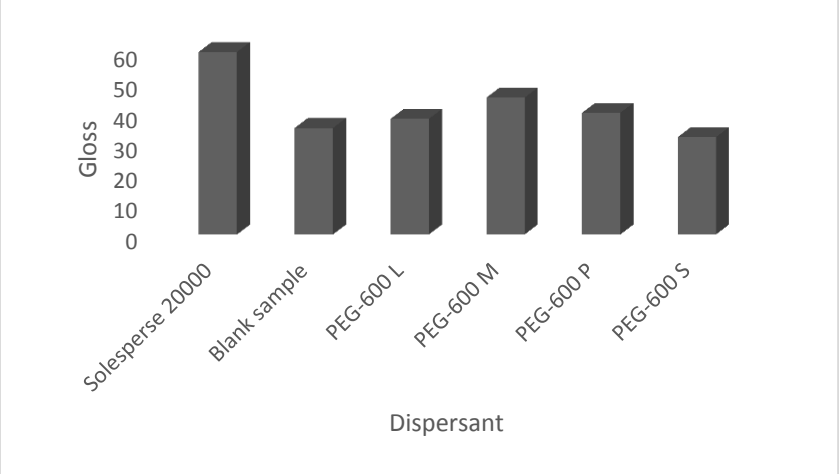

Fig. 8: Gloss of Blue gravure ink were prepared by synthesized dispersants.

Table 4: Transparency of printed films with different pigmented inks prepared by using synthesized dispersants against commercial and blank samples

No.	Dispersant	Yellow	Magenta	Cyan	Black
1	Solsperse® 20000	89.12	73.15	89.45	NA
2	Blank sample	87.85	73.85	89.89	NA
3	PEG600-L	89.11	76.50	89.10	NA
4	PEG600-M	89.97	76.12	91.23	NA
5	PEG600-P	87.85	76.43	90.24	NA
6	PEG600-S	88.52	74.27	89.46	NA

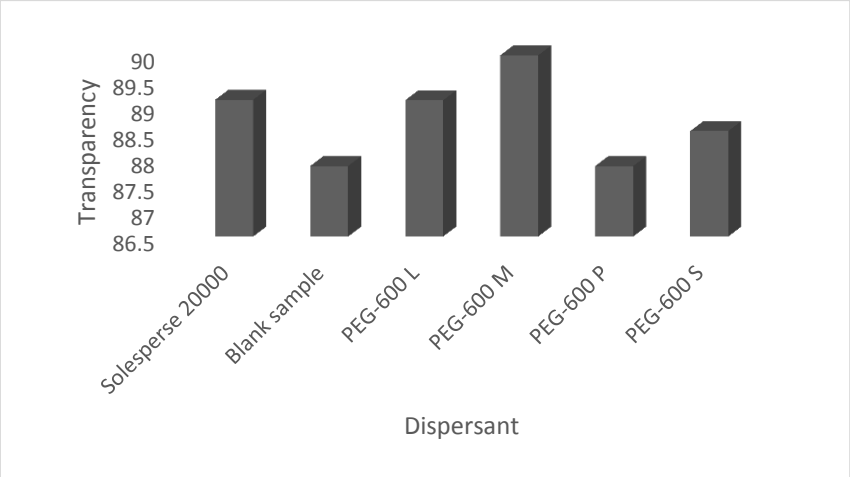

Fig. 9: Transparency of Yellow gravure ink were prepared by synthesized dispersants

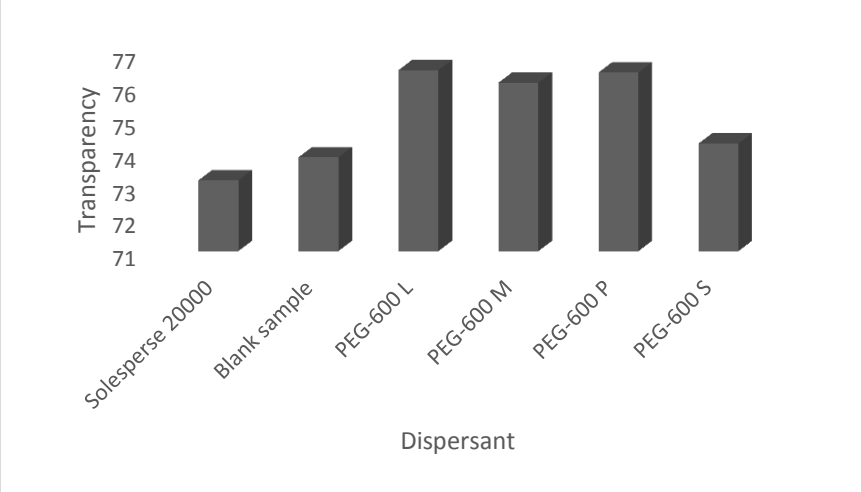

Fig. 10: Transparency of Red gravure ink were prepared by synthesized dispersants

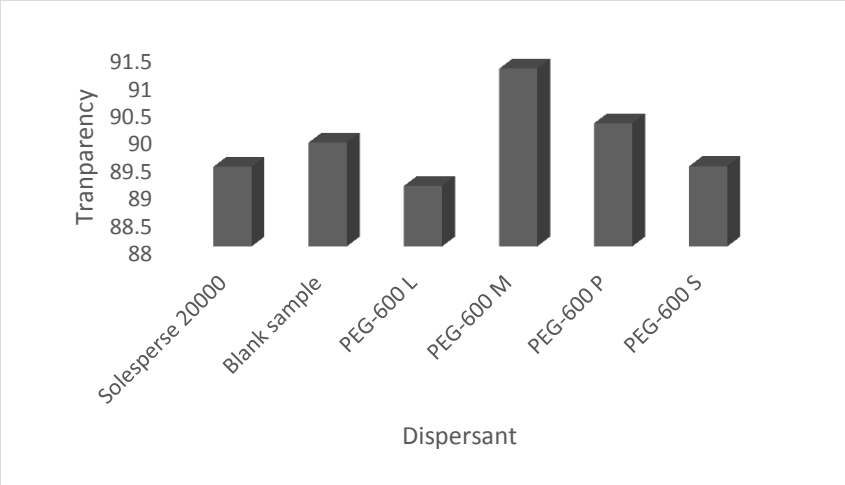

Fig. 11: Transparency of blue gravure ink were prepared by synthesized dispersants

Table 5: Viscosity of different pigmented liquid inks were prepared by using synthesized dispersants against commercial and blank samples

No	Dispersant	Yellow	Magenta	Cyan	Black
1	Solsperse® 20000	120	56	41	45
2	Blank sample	52	48	52	68
3	PEG600-L	77	48	42	59
4	PEG600-M	98	52	68	55
5	PEG600-P	44	52	63	58
6	PEG600-S	78	42	49	70

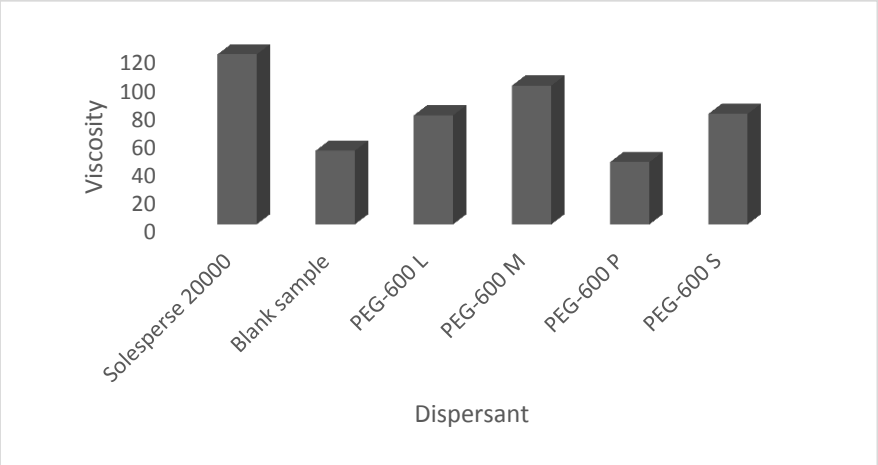

Fig. 12: Viscosity of gravure yellow ink were prepared by synthesized dispersants.

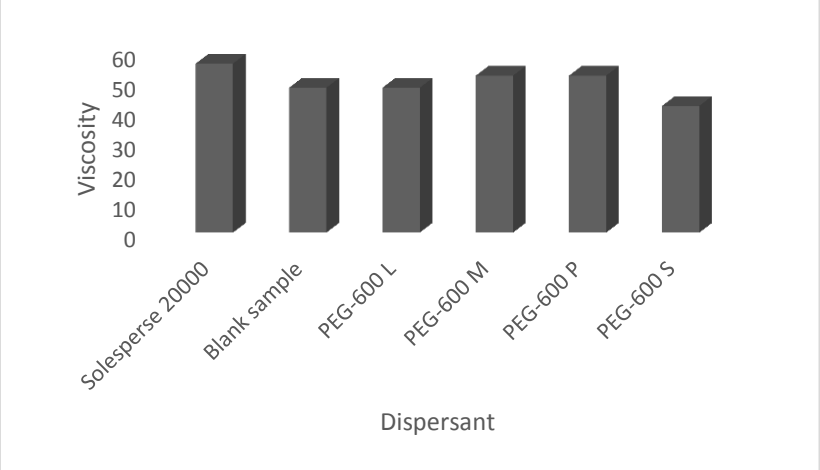

Fig. 13: Viscosity of gravure red ink were prepared by synthesized dispersants.

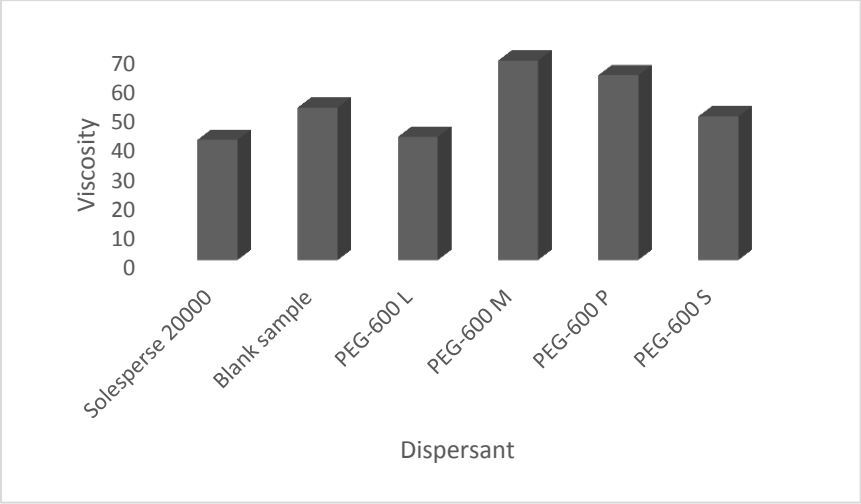

Fig. 14: Viscosity of gravure blue ink were prepared by synthesized dispersants.

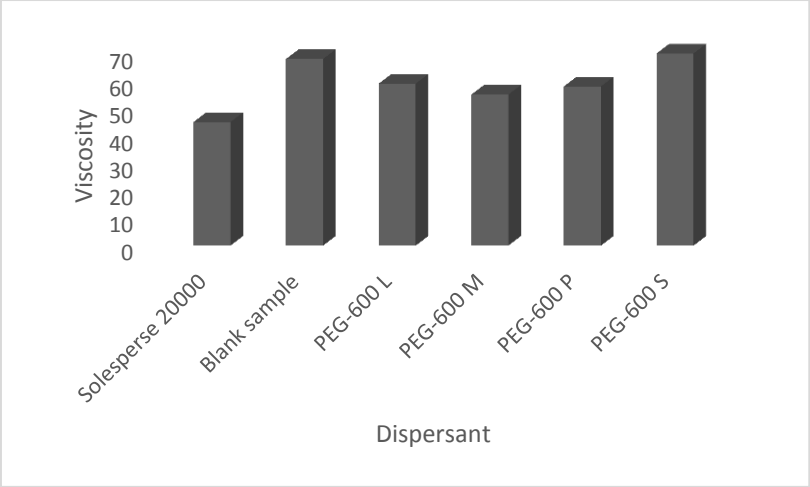

Fig. 15: Viscosity of gravure black ink were prepared by synthesized dispersants.

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