PIGMENTS AND OLIGOMERS FOR INKS - MOVING TOWARDS THE BEST COMBINATION

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ABSTRACT

The formulation of UV curable printing inks depends on several complex factors. If the individual components of the ink are not complementary, then performance problems can arise. One critical combination is that between the pigment and the oligomer. In a new approach to improve understanding of pigment/oligomer interactions, the resources of a pigment manufacturer and an oligomer manufacturer have been combined to investigate the problem. Initial screening of process yellow pigments and several oligomer types highlighted performance variations which were then examined in more detail.

I. INTRODUCTION

According to the independent market research organisation, Frost and Sullivan[1], the radiation curable ink market is forecast to enjoy a ten per cent growth rate. There is also a continual improvement in printing technology. Recent developments in lamp equipment[2] and printing machinery have led to a significant increase in the number of applications and end uses[3]. As a consequence the modern ink maker is facing increased technological demands on their printing ink formulations.

In order to fulfil these demands the printing ink manufacturer has to consider many different parameters including cure response, colour development and ink rheology. One of the most important choices to be made when formulating a UV or EB curable printing ink is that of pigment and oligomer combination. Good pigment dispersion has always been identified as the basis for ink performance and it has been shown that good pigment dispersions give greater flexibility of formulation, particularly those which are printed at low ink film weights[4]. Additionally with the expansion to newer printing methods, different ink rheologies have to be formulated. The combination of pigment and oligomer plays a significant role in determining ink rheology.

This paper examines some of the factors in pigment/oligomer interactions by considering pigment chemistry, pigment treatment and oligomer chemistry. Initially a review of these factors is outlined. Then the effect of pigment/oligomer combinations on ink properties is investigated experimentally. Eight process yellow pigments and five different types of acrylate oligomer were investigated. Raw materials were selected from those typically used in printing ink formulations. From these detailed results several conclusions were drawn which highlight the fact that careful selection of pigment and oligomer for inks can lead to optimised pigment dispersions with better rheology and print behaviour.

II. KEY OLIGOMER CHARACTERISTICS

With respect to oligomer chemistry the following characteristics are relevant to pigment wetting.

(a) Oligomer Chemical Structure

Typically, the main chemical types of radiation curable oligomers are polyesters, epoxides and urethanes where residual hydroxyl groups have been acrylated to provide reactive ethylenic unsaturation. The oligomer backbone and molecular weight distribution can be varied widely. Further chemical modification of the oligomer such as addition of long fatty acid chains, thought to improve pigment-wetting behaviour, may also be applied.

The physical effects of oligomers on the dispersion should be considered. Certain oligomers can be described as 'hard' resin types, which play a significant role in breaking down pigment agglomerates. Molecular structure is also very important for pigment dispersion. For example, a star shaped molecule is believed to be good for pigment dispersion due to its lower viscosity and the effective steric hindrance caused by bulky molecular constituents.[5]

(b) Acid Value

The acid strength of a resin has an effect on its ability to disperse pigment.[5]

(c) Amine Value

Similarly the base strength of a resin is reported to have an effect on pigment wetting ability.[5]

III. KEY PIGMENT CHARACTERISTICS

Key pigment characteristics in the pigment wetting process are outlined below.

(a) Surface Treatment of Pigment

Many pigments are resinated during their manufacture, which has the effect of keeping the particles small and separate. Resination has a number of purposes. It improves colour strength, gloss and transparency by keeping the particles small. In solvent-based ink, resination has a definite advantage of resin solubility in solvent so that the pigment becomes easily stirred in. In UV inks, surface treatment can improve ease of dispersibility in acrylate oligomer as will be seen in this paper.

(b) Pigment Type

Wide ranges of chemistries are used to cover a variety of shades and colours of pigment. Chemical factors are responsible for the characteristics of groups of pigments. These characteristics include shade, colour strength, light fastness, transparency and ease of dispersibility.

(c) Pigment Morphology

The pigment crystal size and shape are important factors in pigment selection. Diarylide yellow pigments are normally brick shaped.[6] The ease with which agglomerates are broken down in the milling stage is also important.

IV. INVESTIGATIVE WORK - EXPERIMENTAL DETAILS

The selected pigments and oligomers were combined to produce mill bases. From those mill bases several parameters were measured before converting each to a standard printing ink.

(a) Millbase Preparation

Millbase concentrates were prepared on the triple roll mill at a standard pigment loading level of 30%. GPTA was used to adjust the millbases to a consistent viscosity of 155 to 190 Pa.s at 25°C. Millbase formulation:

[illegible]	%
Pigment	30
Oligomer	70-x
GPTA	x
Total	100

The dry pigment was mixed firstly by hand with the oligomer/GPTA blend, warmed to 40°C in an oven, mechanically stirred for 3 minutes at 600rpm and given three passes through a triple roll mill.

The millbases were subject to the following tests:

(i) Viscosity
Viscosity was measured at 25°C, using the Haake VT500 cone and plate viscometer, fitted with PK2, 1° cone.

(ii) Yield Value
The yield value, Tau(0), was determined using the Haake VT500 cone and plate viscometer, connected to a PC running software to control the viscometer and perform regression analysis on the resulting shear stress versus shear rate curve.

(iii) Stability
Small samples of each millbase were placed in a 50°C oven for seven days, after which the viscosity was measured. Results are quoted as percentage change from the original viscosity.

(iv) Vertical Flow
Flow length was measured on a vertical glass plane at ambient temperature using 1g of millbase. Prior to the test, the bases were given 50 rubs on an automatic Muller.

(v) Determination of Fineness of Grind

Using a Hegman grind gauge, the fineness of grind was established after three passes on the triple roll mill.[7]

(b) Ink Preparation

(i) Gloss

Millbases were reduced to 18% pigment loading by diluting in GPTA and sensitised with photoinitiator blend:

	%
Millbase	60
GPTA	30
Initiator blend	10
Total	100

Prints were taken on art paper (100gsm) with a Duncan Lynch Proof Printer using 0.4cc of ink. Prints were cured at 50m/min using two 120w/cm MPHg lamps and their gloss measured at 60°. The viscosity of each ink was recorded.

Inks were prepared and printed using millbases diluted in monomer, sensitised with photoinitiator, printed on a non-absorbent substrate, and assessed for visual colour strength, transparency and gloss.

(ii) Colour Strength

Colour strength was measured by Densitometer using DIN standard method at a standard density of 1.25.

(iii) Transparency

Visual assessment of transparency of inks was carried out and compared on an arbitrary scale of 0 to 10, where 0 is most transparent and 10 most opaque.

(iv) Gloss

The instrumental gloss reading was taken from weighed prints on a non absorbent substrate.

V. RESULTS AND DISCUSSION

The criteria for selecting the oligomer type were based upon chemistry and application end use. The pigments were also selected on this basis. Pigments I to V were designed for a variety of inks whilst pigments VI to VIII were specifically intended for liquid inks. The table below describes the materials used.

Table I. Oligomers used

Oligomer	Molecular Weight	Viscosity (Pa.s) @25°C
Urethane Acrylate	900	100 - 140
Fatty Acid Modified Epoxy Acrylate	580	120 - 200
Epoxy Acrylate	550	25 - 45
Polyester Acrylate - Type 1	1200	20 - 40
Amine Modified Urethane Acrylate	1200	40 - 80

Table II Pigments used

Pigment	Description
Yellow I	Opaque CI Pigment Yellow 13 designed for oil and liquid inks
Yellow II	CI Pigment Yellow 174 for oil inks
Yellow III	CI Pigment Yellow 188 for oil inks
Yellow IV	Transparent CI Pigment Yellow 13 for oil inks (some liquid/packaging use)
Yellow V	CI Pigment Yellow 13 for oil, liquid/packaging and water-based inks
Yellow VI	CI Pigment Yellow 13 for liquid/packaging ink, modified for improved flow
Yellow VII	CI Pigment Yellow 13 for liquid/packaging ink, modified for improved dispersibility
Yellow VIII	CI Pigment Yellow 13 for liquid/packaging ink only

Table III Dispersion Results

	Urethane Acrylate	Fatty Acid Modified Epoxy Acrylate	Epoxy Acrylate	[illegible] Acrylate Type I	[illegible]
Yellow I					
Millbase Viscosity (Pa.s)	185.0	192.0	170.0	163.0	106.0
Millbase Vertical Flow (mm)	0.0	0.0	0.0	0.0	0.0
Millbase Yield Value (Pascals)	780.0	930.0	2150.0	750.0	670.0
Millbase Oven Stability (%inc. in viscosity)	23.0	37.0	19.0	48.0	30.0
60° Print Gloss	24.0	17.0	22.0	19.0	18.0
Transparency	5	4	5	5	7
Gloss	57	55	44	43	32
Colour Strength at 1.25g/m^2					
density	1.28	1.31	1.3	1.29	1.31
parts	100	107	105	103	106
Yellow II					
Millbase Viscosity (Pa.s)	180.0	180.0	160.0	171.0	168.0
Millbase Vertical Flow (mm)	0.0	0.0	0.0	0.0	0.0
Millbase Yield Value (Pascals)	2550.0	2950.0	4180.0	2330.0	1620.0
Millbase Oven Stability (%inc. in viscosity)	14.0	27.0	-7.5	19.0	22.0
60° Print Gloss	24.0	22.0	21.0	19.0	23.0
Transparency	5	5	5	5	5
Gloss	61	65	50	51	39
Colour Strength at 1.25g/m^2					
density	1.31	1.28	1.26	1.25	1.31
parts	107	98	95	92	105
Yellow III					
Millbase Viscosity (Pa.s)	168.0	175.0	183.0	160.0	140.0
Millbase Vertical Flow (mm)	10.0	10.0	0.0	10.0	10.0
Millbase Yield Value (Pascals)	480.0	640.0	1130.0	600.0	610.0
Millbase Oven Stability (%inc. in viscosity)	36.0	29.0	9.0	25.0	25.0
60° Print Gloss	37.0	21.0	25.0	35.0	27.0
Transparency	5	5	5	5	5
Gloss	76	76	65	68	56
Colour Strength at 1.25g/m^2					
density	1.26	1.26	1.26	1.23	1.29
parts	95	96	98	87	101
Yellow IV					
Millbase Viscosity (Pa.s)	155.0	165.0	157.0	177.0	129.0
Millbase Vertical Flow (mm)	0.0	0.0	0.0	0.0	0.0
Millbase Yield Value (Pascals)	3490.0	2310.0	2770.0	2330.0	1900.0
Millbase Oven Stability (%inc. in viscosity)	7.0	47.0	>125	4.0	36.0
60° Print Gloss	24.0	17.0	15.0	25.0	19.0
Transparency	5	5	5	5	5
Gloss	57	60	50	51	38
Colour Strength at 1.25g/m^2					
density	1.32	1.27	1.29	1.21	1.32
parts	108	98	103	83	108

Table III Dispersion Results (continued)

	Urethane Acrylate	Fatty Acid Modified Epoxy Acrylate	Epoxy Acrylate	Polyester Acrylate Type I	Amine Modified Urethane Acrylate
Yellow V					
Millbase Viscosity (Pa.s)	190.0	158.0	185.0	160.0	105.0
Millbase Vertical Flow (mm)	0.0	0.0	0.0	0.0	0.0
Millbase Yield Value (Pascals)	1300.0	2040.0	2980.0	510.0	920.0
Millbase Oven Stability (%inc. in viscosity)	1.0	77.0	23.0	17.0	46.0
60° Print Gloss	23.0	14.0	14.0	23.0	17.0
Transparency	5	4	4	5	4
Gloss	55	50	40	41	22
Colour Strength at 1.25g/m^2					
density	1.28	1.36	1.3	1.33	1.34
parts	98	120	104	111	114
Yellow VI					
Millbase Viscosity (Pa.s)	168.0	153.0	189.0	166.0	175.0
Millbase Vertical Flow (mm)	5.0	20.0	5.0	15.0	15.0
Millbase Yield Value (Pascals)	1000.0	630.0	750.0	230.0	1040.0
Millbase Oven Stability (%inc. in viscosity)	18	49	61	26	8
60° Print Gloss	28.0	19.0	22.0	35.0	24.0
Yellow VII					
Millbase Viscosity (Pa.s)	175.0	186.0	163.0	163.0	124.0
Millbase Vertical Flow (mm)	5.0	5.0	0.0	5.0	5.0
Millbase Yield Value (Pascals)	820.0	700.0	1130.0	610.0	1890.0
Millbase Oven Stability (%inc. in viscosity)	13.0	58.0	58.0	34.0	39.0
60° Print Gloss	23.0	30.0	18.0	46.0	19.0
Yellow VIII					
Millbase Viscosity (Pa.s)	182.0	190.0	177.0	158.0	156.0
Millbase Vertical Flow (mm)	5.0	5.0	0.0	5.0	5.0
Millbase Yield Value (Pascals)	1630.0	1300.0	1580.0	1170.0	1640.0
Millbase Oven Stability (%inc. in viscosity)	9.0	54.0	17.0	33.0	40.0
60° Print Gloss	18.0	19.0	17.0	30.0	22.0

Note

The pigments VI to VIII showed difficulties in dispersion that indicated they should not proceed to the ink testing stage.

Observations and Conclusions

(i) Colour development was as expected for all pigments, comparable to that expected in conventional lithographic oil based systems. All dispersions had a grind particle size of less than five microns on the Hegman grind gauge.

(ii) The results show a wide range of physical properties with different pigment/oligomer combinations. There are noticeable variations in viscosity, yield value and flow. This would render some combinations more suited to specific ink types. The best flow is obtained with pigments III and VI.

(iii) The amine modified urethane acrylate showed little overall benefit with any pigment type

(iv) As stated previously the pigments designed for liquid inks could only be used with difficulty because of predispersion and filtering problems.

(v) The urethane acrylate type I and polyester acrylate tend to give better rheological properties.

VI. CONCLUSIONS

The test results show that by varying pigment and oligomer type a variety of different ink rheologies and performance can be achieved. This can assist in selection for different ink applications. The initial conclusion is that urethane acrylate and polyester acrylate type I provide the best starting material, particularly when combined with pigments III or VI.

Some consideration has been given as to why these particular materials perform better in a specific combination. One suggestion is that performance variation could be attributable to differing polarities and the compatibility within the pigment and oligomer interface. This suggestion allied to the evidence that improved pigment wetting benefits ink performance will be used to develop the themes initiated in this paper and reported at a later stage.

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