

Can A Polyamide Resin Be Formulated Into A High-Performance Digital Printing Ink?

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Abstract

Dimer acid-based polyamides are resins of choice for flexographic inks printed on non-porous substrates, especially packaging films and foils. But can they work in inks designed for wide-format printers? To answer this question, we determined the behavior of carefully chosen polyamide resins in non-conventional solvents and solvent blends and tested the most promising resins and blends in basic ink formulations, obtaining data on their viscosity, stability, jetting behavior, drying rate, rub-resistance, and adhesion.

Introduction

Formulation of drop-on-demand (DOD) inks suitable for printing on a variety of non-porous media by wide-format digital printers for use in in- and outdoor display, marking, and imaging applications requires a versatile resin having adhesion, abrasion-resistance, pigment compatibility and low solution viscosity. Could that resin be a dimer acid-based polyamide? These clear, tough, non-tacky thermoplastic solids exhibit low solution viscosities in lower alcohols. They have excellent adhesion to many surfaces and stabilize many pigments in flexographic ink solvents. Oligomeric versions are used in hot-melt digital inks¹⁻³ and others have been claimed for use in CIJ inks.⁴ We thought they would make excellent binders for solvent DOD jet inks applied to plastics and other non-porous surfaces. To support or refute this contention, we had to answer this series of questions:

- Do these resins dissolve in solvents favored now by digital ink makers? If not, what solvents might be used instead?
- Are pigmented inks made with polyamides stable?
- Do these inks jet satisfactorily?
- What is the quality of the image formed by jetting such ink?
- How rapidly do they dry on plastic film?
- Does the dried ink have good adhesion, rub-resistance and water-resistance?

Choosing Resin and Solvent

To choose appropriate resins to study, we screened the large number of polyamides sold into the flexographic ink market by Arizona Chemical and available to us by synthesis in our laboratory for candidates of low solution viscosity, moderately high softening point, good clarity, better than normal solubility, and excellent adhesion to polyolefin films, glass, and metal. This work led us to select two resins designated here by notebook page numbers 018-107 and 018-129 and having the properties listed in Table 1. Because polyamides as a class of polymer are not readily soluble in organic solvents or water, we expected to have difficulty selecting a good ink carrier. However, in contrast to crystalline fiber-forming polyamides such as nylon, polyamides containing the dimer acid moiety are largely amorphous and are soluble in mixtures of aromatic hydrocarbons such as toluene and a lower aliphatic alcohol such as 1-propanol. Flexographic ink makers formulate mainly with alcohols mixed with aliphatic esters such as ethyl acetate. These solvents are too volatile and/or toxic for use in digital printing inks except for continuous ink jet inks. The solvents used in current DOD inks are glycol ethers, ketones and acetates for which polyamides have little or no affinity. We sought new solvents meeting most or all of the criteria listed in Table 2.

Table 1. Properties of the Resins of This Study

Resin Designation	Polyamide #018-107	Polyamide #018-129
Softening Point	109°C	114°C
Acid Number	4.6	3.5
Amine Number	1.9	2.2
Color	Light amber	Light amber
Viscosity at 130°C	450 cP	1,700 cP
Solubility in Water	Negligible	Negligible
Mol. Weight (Mn)	1,800	3,000
Mol. Weight (Mw)	4,400	13,000
Appearance, feel	Clear, hard	Clear, hard

A compilation of properties of a few of the solvents we tested is in Table 3. Polyamide resins were not soluble or stable in two representative glycol ethers, dipropylene glycol monomethyl ether (DPM) and 2-methoxy-1-propanol (2-MP), or a representative lactate ester, ethyl lactate (EL), or a representative ketone, cyclohexanone (CHN). No other single solvent appeared to be ideal. Amides, as might be expected, are good solvents for polyamides and of these N-methylpyrrolidinone (NMP) is the best because it is bland in odor, widely regarded as low in toxicity, and has a high flash point. It dries slowly, however, and dissolves some adhesives. Dimethyl acetamide has a lower viscosity, acceptable flash point, and pleasant odor but suspect toxicity. Alcohols less volatile than 1-propanol and ethanol, including 1-hexanol and 2-ethyl-1-hexanol, are acceptable but these solvents have higher viscosities than amide, ether, ketone, and ester solvents.

Table 2. Wide Format Ink Solvent Criteria

Criterion Type	Criterion Level Desired	Reason for Criterion
Flash Point	Near or above 142°F	Allows shipment as non-hazardous
Evaporation	As fast as possible	Faster drying, increased press speed
Viscosity	As low as possible	Increased formulating flexibility
Stability	Fluid, clear if chilled	Gelation/precipitation when shipped
Cost	Same as ones used now	No increased cost is desired.
Aggressiveness	No worse than ones used now	Could attack print head adhesives
Toxicity	Low hazard, "green" image	Toxic or unpleasant solvents might require special ventilation for use
Odor	Pleasant or bland	

Table 3. Candidate Solvents for Formulating Low Volatility Jet Inks

Solvent Name	Flash Point (°F)	Viscosity (cP, 25°C)	Evaporation Rate ^a	Density (25°C)	Odor
Hexanol	140	ca. 6	0.05	0.814	Doughy
EL	120	2.4	0.21	1.042	Fruity
DPM	172	0.95	0.03	0.951 ^b	Bland
CHN	116	2.0	0.29	0.947	Cheesy
d-L	115	ca. 1.5	n.a.	0.844	Orange
S142	145	ca. 1.5	n.a.	0.782 ^c	Bland
NMP	196	1.7	0.06	1.040	Bland

^aRelative to n-butyl acetate ^bat 68°F ^cat 60°F

Key to formulating polyamides is use of blends of amide or alcohol solvent and hydrocarbon co-solvent. Poor solvents by themselves, hydrocarbons increase solution stability and decrease drying times, odor, solvent aggressiveness, cost, and solution viscosity of an amide or alcohol solution. We give data here for just three of many

possible hydrocarbons, namely, Solvent 142 (Ashland) a mineral spirit (S142), d-limonene (d-L), which is distilled from orange oil, and terpinolene (T90), available from IFF. Any mineral spirit can substitute for S142 and other terpenes for d-L or T90 to adjust volatility and viscosity. Use then of blends of these solvents leaves open numerous options for the ink maker to adjust flash point, evaporation rate, viscosity and odor.

Solution Viscosity And Stability

We tested solvents by preparing resins solutions of 10-25%, observing their clarity and viscosity (values in this paper are reported in cP measured at 25°C). Because a characteristic of polyamide solutions is spontaneous transformation into clear, homogenous gels on cooling and standing at room temperature, we tested solutions for gel resistance by subjecting them to 0°C for 24h and then warming them to 23°C. If after warming the solution was not clear, fluid, and homogeneous we judged it a failure (Fd). If it was not clear and fluid at 0°C but became so after warming, we judged it had "recovered" (OK). The best result (Exc) was it remained clear and fluid even at 0°C. Selected results with the more promising solvents are in Tables 4-7. For preparing the inks described here we elected to use the solvent blends consisting of d-L, 2-MP or 1-butanol and NMP of Table 8.

Table 4. Viscosity and Solution Stability of Resin #018-107 in Blends of Hexanol and Aliphatic Hydrocarbon

Resin Concentration is 20% ^a							
Hexanol	50	50	50	50	40	30	20
S142	50	25	25	25	60	70	80
DPM	-	25		-	-	-	-
EL	-	-	25	-	-	-	-
CHN	-	-	-	25	-	-	-
Viscosity	Nd	16.8	15.2	13.0	13.8	13.5	Gel
Stability	Exc	OK	Exc	OK	OK	OK	-

Table 5. Viscosity and Solution Stability of Resin #018-107 in Blends of NMP and Terpene Hydrocarbons

Resin Concentration is 25% ^a					
NMP	60	50	40	30	20
d-L	-	-	-	-	80
T90	40	50	60	70	-
Viscosity	14.6	15.9	n.d.	15.4	14.3
Stability	Exc	Exc	OK	OK	OK

Table 6. Viscosity and Solution Stability of Resin #018-129 in Blends of Alcohols and Hydrocarbon

Resin Concentration is 20% ^a				
Hexanol	60	50	40	30
S142	40	50	60	70
Viscosity	23.7	21.6	21.5	20.8
Stability	Exc	Exc	OK	Fd

Table 7. Viscosity and Solution Stability of Resin #018-129 in Blends of Alcohols and Hydrocarbon

Resin. (Wt% ^a)	20	15	15	15	15	10	10
EL	25	50	25	25	50	50	25
d-L	50	25	50	25	50	25	50
CHN	25	25	25	50	-	25	25
Viscosity	20.2	11.1	11.4	10.7	12.0	6.4	6.0
Stability	OK	OK	OK	Fd	Exc	Exc	Exc

^aSolvent amounts expressed as weight % on total solvent amount.

Table 8. Solvent Blends For Ink Formulation

Solvent	Blend #1	Blend #2
d-Limonene	47.5	47.5
2-Methoxy-1-Propanol	47.5	-
1-Butanol	-	47.5
N-Methylpyrrolidinone	5.0	5.0

Table 9. Test Dispersions of Pigments

Components ^a	Disp#6	Disp#7	Disp#8	Disp#9
Blend #1	80	90	80	80
Resin 018-107	10	-	10	-
Resin 018-129	-	-	-	10
Regal Black 660	10	-	-	10
Irgalite Cyan	-	-	10	-
Microlith Black	-	10	-	-
Viscosity	15.1	25.7	5.5	6.9

^aComposition amounts given in weight%

Dispersion and Ink Formulations

We incorporated the two polyamide resins into dispersions containing Regal Black 660, a non-predispersed carbon pigment, and Blend #1 using a high shear, high speed mixer followed by a horizontal mill filled with 1 mm zirconium silicate beads and operating at 3,000 rpm for 2h. Normally a polymeric dispersant would be used to stabilize this pigmented system, however we used none in order to observe the pigment wetting performance of the polyamides. Unexpectedly, the higher-molecular weight resin yielded the lower viscosity dispersion, suggesting that it is an excellent pigment dispersant. We also made dispersions using a cyan pigment, Irgalite Blue GLVA, and a pre-treated black pigment, Microlith Black C-A (Ciba), under the same milling conditions but in the latter case without polyamide. Formulations for all these dispersions are in Table 9. To improve the hardness/durability of the ink, we sought to add three known hard resins, namely Joncryl 682 (S.C. Johnson), Sylvares TP7042 (Arizona), and a nitrocellulose. We made varnishes with the former two but found that the latter was not compatible with Blend#1.

To make test inks we prepared letdown varnishes of 25% resin/hardener in Blends #1 or #2 (containing either 2-MP or butanol) and then added these to the appropriate dispersions, adding NMP-rich solvent as required to achieve a viscosity of 8-13 cP and an NMP level of about 12%. We

brought the pigment concentration in each ink to 5.0%. The inks containing hardener resins contained an equal weight of polyamide #018-107. The amounts of each of the components in each of the inks are in Tables 10 (for the formulations containing resin #018-107) and Table 11 (for inks containing resin #018-129 and hardeners). We used near infrared sedimentometry to assess the stability of all of our test inks. In all cases there was negligible settling of the pigment over the 8 h test period. All of the test inks had dwell times less than the 180 s of the control ink but dried faster than the control ink, which required 610 s.

Table 10. Inks Containing Polyamide #018-107

Ink Code No.	Ink#33	Ink#20	Ink#27	Ink#46
Resin (wt%).	14.9	9.9	9.9	21.0
Pigment type	Regal 660	Microlith Black		Irgalite Cyan
Pigment (wt%)	5.0	5.0	5.0	5.0
Alcohol type	2-MP	2-MP	Butanol	2-MP
Alcohol (wt%)	34.1	36.2	40.4	31.0
NMP (wt%)	12.0	12.8	4.3	12.0
Filter pads ^a	2	1	2	1
Viscosity (cP)	8.6	9.4	12.5	12.9
Surface tension ^b	31.0	31.0	28.5	32.0
Filtration test ^c	24	35	106	35
Load, prime	All were equally easy			
Print temp. (°C)	35	30	35	30
Dwell time ^d	50	40	20	60
Dry time ^e	350	100	80	400

Table 11. Inks Containing Resin #018-129 or Hardeners

Resin Type	#018-129	1:1 J-682 #018-107	1:1 S-TP #018-107
Ink Code No.	Ink#18	Ink#23	Ink#35
Pigment type	All with Microlith Black		
Resin (wt%)	7.50	9.88	9.88
Pigment (wt%)	5.0	5.0	5.0
2-MP (wt%)	37.2	40.4	40.4
NMP (wt%)	13.1	4.3	4.3
Filter pads ^a	1	1	1
Viscosity (cP)	12.6	9.72	9.56
Surface tension ^b	30.5	30	30
Filtration test ^c	29 s	27 s	42 s
Load, prime	All were equally easy		
Print temp. (°C)	40	30	35
Dwell time ^d	30 s	60 s	90 s
Dry time ^e	80 s	110 s	150 s

^ano. of 1.0µm filter pads needed to filter batch of ink. ^bdynes/cm ^ctime for 15ml to pass a 1.0µm filter pad. ^dtime until ink channels are noticeably missing. ^etime until ink is noticeably tack-free.

We degassed the inks by a 20 min. helium purge prior to loading a Trident Ultrajet 96/32 print head and jetting them on an untreated vinyl of the type used in wide format printing. We then assessed print quality and performance characteristics of the ink. A polymer/butyl lactate ink developed for use on vinyl served as reference. Results are also

in Tables 10 and 11. We observed the ease of loading and priming of the print head, a good indicator as to whether or not an ink will jet well, the face plate dwell time, and the dry time. All these inks gave consistent results after priming and adjusting the print head temperature for optimal jetting.

Print Testing, Adhesion and Print Quality

To evaluate print adhesion and durability, we carried out tests on solid prints and dot patterns of each ink jetted and allowed to dry thoroughly on four substrates, namely, low-density polyethylene (LDPE), Melinex, a polyethylene terephthalate (PET), glass and aluminum foil (shiny side). These tests are as follows: Test A - fingernail scratch resistance, Test B - removal of the print by applied Scotch tape; Test C - resistance to rubbing 100 times with a dry lab wipe; Test D - resistance to rubbing 100 times by a wet lab wipe; and Test E - overall quality of dot formation by visual inspection. For each we gave a "grade" based on ink removal, from 1 to 5, where 1 indicates poor, 5 excellent. The results are in Tables 12-15.

Table 12. Print Quality Test Results on LDPE

Test	Ink #33	Ink #20	Ink #27	Ink #46	Ink #18	Ink #23	Ink #35	Control
A	3	1	2	4	-	1	1	1
B	4	2	4	5	-	1	2	2
C	1	1	1	2	-	1	1	1
D	5	1	5	4	-	5	5	4
E	5	4	3	5	-	4	4	4

Table 13. Print Quality Test Results on PET

Test	Ink #33	Ink #20	Ink #27	Ink #46	Ink #18	Ink #23	Ink #35	Control
A	1	2	2	3	4	4	4	1
B	5	5	3	5	4	3	4	3
C	2	2	2	1	1	4	3	1
D	5	5	5	5	2	5	5	5
E	5	3	3	4	3	3	3	3

Table 14. Print Quality Test Results on Glass

Test	Ink #33	Ink #20	Ink #27	Ink #46	Ink #18	Ink #23	Ink #35	Control
A	2	2	1	1	1	5	1	1
B	5	4	4	4	4	5	4	4
C	3	2	2	2	1	5	1	1
D	1	1	1	1	2	1	1	1
E	4	3	3	5	4	3	3	3

Table 15. Print Quality Test Results on Aluminum

Test	Ink #33	Ink #20	Ink #27	Ink #46	Ink #18	Ink #23	Ink #35	Control
A	4	5	5	4	-	5	5	2
B	5	5	5	4	-	3	4	5
C	3	2	4	3	-	5	5	1
D	1	5	5	5	-	5	2	2
E	5	3	4	5	-	3	4	3

Encouragingly, the average score of the test inks in each performance test for all four substrates was higher than the control ink score with the exception of B/Scotch tape adhesion on aluminum, a test in which the control scored a "5" and the average of the test inks was 4.3. In general, E/print quality was good-to-excellent and D/wet rub was excellent except on glass. C/Dry rub, a particularly severe test, was low for all of the inks, except on aluminum, where most of the test inks (average 3.7) easily out-performed the control. These promising results obtained even though we did not attempt to optimize any of the formulations for any of the substrates.

Modification of the polyamide inks with hardeners improved their performance in some respects. Addition to the initial ink formulations of J-682 improved dwell time and increased dry time compared to polyamide #018-007 alone. The S-TP7042 had a greater effect increasing dry time and dwell time than did the J-682. Print performance test scores of inks made with hardeners were slightly higher than the all-inks average with the J-682 ink having a slight edge in performance on glass and aluminum over the S-TP7042 ink.

We took high-speed photographs of jets in flight of Ink #33 and Ink #46 to check the quality of droplet formation. This occurred smoothly, by elastic rebound of the initially formed columnar jet of ink, without any shattering or spray.

Conclusion

Low viscosity inks with high polyamide resin content which jet at near-ambient temperatures are well behaved when formulated with carriers containing significant amounts of an alcohol/amide solvent and a hydrocarbon co-solvent. Jet print testing versus a conventional ink of a number of trial polyamide inks showed these to have fast drying times but lower faceplate dwell times. Addition of a compatible hardener resin improved dwell times and also some ink performance characteristics. Inks containing the lower molecular weight polyamide gave the most consistent jetting so that higher molecular weight resins may not be preferred. All inks showed good print quality on the four test substrates and many out-performed the control ink.

The answer, then, to the question posed by the title of this paper is "yes". We do not mean to say the inks described here are optimal; rather, these promising ink formulations should be an encouragement to ink makers to use polyamide resins and, guided by our experience, improve on them.

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Biographies

Dr. Mark Pavlin has done product development work in tree-derived chemicals since obtaining a Ph.D. in Organic Chemistry from the University of Illinois in 1977. He is presently Principal Scientist and Team Leader of the Exploratory Development Group at Arizona.

James Fox joined Xennia in 1996 as Inkjet Scientist and became R&D Director in 1999. He has been involved with all forms of inkjet technology, developing a wide range of products for a variety of new and existing applications. He

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Jagvi Patel joined Xennia in August 2000 as an Inkjet Scientist working mainly as project leader for development of UV curable systems. She graduated from King's College, London University first with a BSc Honours degree in Chemistry and Mathematics and then with a Ph.D. degree in Physical Organic Chemistry.

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