



Faculty of Women for
Arts, Science and Education
Cairo, Egypt

Synthesis and characterization of polymeric modified aldehydes for printing inks applications

**A Thesis Submitted for
Partial Fulfilment of the Requirements for the
Degree of Master of Science
(Organic Chemistry)**

Presented by

Ahmed Sayed Ahmed

(B.Sc. Chemistry 2008)

Supervisors

Prof. Dr. Nadia G. Kandile

Prof. of Organic Chemistry

Faculty of Women for Arts, Science and Education

Ain Shams University, Egypt

Prof. Dr. Nabel A. Negm

Prof. of Applied Petrochemicals

Egyptian Petroleum Research Institute (EPRI)

2018



Faculty of Women for
Arts, Science and Education
Cairo, Egypt

Synthesis and characterization of polymeric modified aldehydes for printing inks applications

A Thesis Presented

To

**Faculty of Women for Arts, Science and Education
Ain Shams University**

By

Ahmed Sayed Ahmed

Submitted for

Degree of Master of Science

(Organic Chemistry)

2018



Faculty of Women for
Arts, Science and Education
Cairo, Egypt

Student Name : Ahmed Sayed Ahmed

Scientific Degree : B.Sc.

Department : Chemistry

Name of Faculty : Faculty of Science

University : Ain Shams University

B.Sc. Graduation Year : 2008

M.Sc. Graduation Year : 2018



Faculty of Women for
Arts, Science and Education
Cairo, Egypt

Synthesis and characterization of polymeric modified aldehydes for printing inks applications

Supervised by:

Prof. Dr. Nadia G. Kandile

Prof. of Organic Chemistry

Prof. Dr. Nabel A. Negm

Prof. of Applied Petrochemicals

Approved

Approved

Head of Chemistry Department

Prof. Dr.

ACKNOWLEDGMENT

First and foremost, thanks be to the almighty (**ALLAH**) for limitless help and guidance and peace be upon his prophet.

I would like to express my deep respect, and sincere appreciation to Prof. Dr. Nadia Gharib Kandile, Prof. of Organic Chemistry (Faculty of Women for Arts, Science and Education, Ain Shams University) for her sincere supervision, for her continuous advice, guidance, respective suggestion, support which she offered me through progress and finishing this work.

I really appreciate the efforts of Prof. Dr. Nabel Abdel Moneem Negm Prof. of Petrochemicals (Egyptian Petroleum Research Institute) for the supervision, valuable assistance and guidance during this work.

My deep thanks to Dr. Ahmed Abo El-Wafa the owner of Degla Chemicals Company for his support and continuous help.

I would also like to thank my family for their support and encouragement.

My special gratefulness to my wife Eng. Esraa Khairy for her encouragement, support, and patience to fulfill my study.

I would like to acknowledge the funding support allowed by DEGLA chemicals Co. in addition to the laboratory research facilities made available to accomplish this project.

Finally, I would like to thank members of the research team, Mahmoud Abdel Rahman, Mohamed Hashem & Mohammed Abdel Aziz for creating an enjoyable working environment.

TABLE OF CONTENTS

Content	Page
LIST OF FIGURES	IX
LIST OF TABLES	XIII
LIST OF SCHEMES	XIV
LIST OF ABBREVIATIONS	XV
AIM OF THE WORK	XVI
ABSTRACT	XVII
SUMMARY	1
CHAPTER I	
INTRODUCTION	
1. Introduction	4
1.1.Industrial Inkjet	6
1.2.Types of Inkjet inks	6
1.3.Main advantages & disadvantages of solvent based inkjet inks.	8
1.3.A. Advantages	8
1.3.B. Disadvantages	8
1.4.Inkjet inks raw materials	9
1.5.Nano-sized pigments	12
1.6.Inkjet dispersants chemistry	13
1.7.Mannich reaction	20
1.8.Literature survey	22
CHAPTER II	
EXPERIMENTAL	
2. Experimental	38
2.1.Materials	39
2.2.Instruments	39
2.3.Methods	40
2.3.1. Testing	40
2.3.2. Synthesis	40
2.3.3. Inkjet ink formulation	45

CHAPTER III	
RESULTS AND DISCUSSION	
3. Results & discussion	46
3.1.Theory of work	47
3.1.A. Dispersants (R1–R5)	47
3.1.B. Dispersants (C1–C5)	49
3.1.C. Dispersants (A1–A5)	52
3.2.FTIR results	54
3.2.A. Dispersants (R1–R5)	54
3.2.B. Dispersants (C1–C5)	55
3.2.C. Dispersants (A1–A5)	57
3.3.GPC results	59
3.3.A. Dispersants (R1–R5)	60
3.3.B. Dispersants (C1–C5)	61
3.3.C. Dispersants (A1–A5)	63
3.4.Particle size results	65
3.4.A. Cyan 15:3 Inkjet inks	65
3.4.B. Black 7 Inkjet inks	70
3.5.Optical properties	75
3.5.A. Cyan 15:3	75
3.5.B. Black 7	77
CONCLUSIONS	85
REFERENCES	87
ARABIC SUMMARY	i

LIST OF FIGURES

Figure No.	Title of figure	Page
Figure (1)	Difference in droplet ejection between (A) continuous inkjet printing head and (B) drop on demand printing head	6
Figure (2)	A generic classification of inkjet inks can be scheme	7
Figure (3)	Difference in light reflection between pigment and dye based inks	11
Figure (4)	Length scale encountered in inkjet printing industry	12
Figure (5)	p-Aminobenzoic acid-formaldehyde resin	32
Figure (6)	FT-IR spectra of dispersants (R1–R5)	55
Figure (7)	FT-IR spectra of dispersants (C1 – C5)	57
Figure (8)	FT-IR spectra of dispersants (A1–A5)	59
Figure (9)	GPC chromatogram for dispersants (R 1 – R 5)	61
Figure (10)	GPC chromatogram for dispersants (C1 – C5)	63
Figure (11)	GPC chromatogram for dispersants (A1 – A5)	64
Figure (12)	Particle size of fresh cyan 15-3 inkjet ink dispersants (R1 – R5) & BASF standard	67
Figure (13)	Particle size after stability of cyan 15-3 inkjet ink dispersants (R1 – R5) & BASF dispersant	67
Figure (14)	Particle size of fresh cyan 15-3 inkjet ink dispersants (C1 – C5) & BASF dispersant	68
Figure (15)	Particle size after stability of cyan 15-3 inkjet	68

	ink dispersants (C1 – C5) & BASF dispersant	
Figure (16)	Particle size of fresh cyan 15-3 inkjet ink dispersants (A1 – A5) & BASF dispersant	69
Figure (17)	Particle size after stability of cyan 15-3 inkjet ink dispersants (A1 – A5) & BASF dispersant	68
Figure (18)	Particle size of fresh black 7 inkjet ink dispersants (R1 – R5) & Tianlong dispersant	72
Figure (19)	Particle size after stability of black 7 inkjet ink dispersants (R1 – R5) & Tianlong dispersant	72
Figure (20)	Particle size of fresh black 7 inkjet ink dispersants (C1 – C5) & Tianlong dispersant	73
Figure (21)	Particle size after stability of black 7 inkjet ink dispersants (C1 – C5) & Tianlong dispersant	73
Figure (22)	Particle size of fresh black 7 inkjet ink dispersants (A1 – A5) & Tianlong dispersant	74
Figure (23)	Particle size after stability of black 7 inkjet ink dispersants (A1 – A5) & Tianlong dispersant	74
Figure (24)	Interaction forces of dispersants R4 & R5 with cyan 15:3 pigment	79
Figure (25)	Interaction forces of dispersants R-4 & R-5 with black 7 pigment	80
Figure (26)	Interaction forces of dispersants C-4 & C-5 with cyan 15:3 pigment	81
Figure (27)	Interaction forces of dispersants C-4 & C-5 with black 7 pigment	82
Figure (28)	Interaction forces of dispersants A-4 & A-5 with cyan 15:3 pigment	83

Figure (29)	Interaction forces of dispersants A-4 & A-5 with black 7 pigment	84
Figure (30)	Salt formation of p-ammonium benzoate	84

LIST OF TABLES

Table No.	Title of table	Page
Table (1)	Examples of various technologies that implement inkjet	5
Table (2)	Typical stabilizing tails and anchor groups for sterically stabilized pigments.	14
Table (3)	Inkjet ink formulation used for testing the dispersants prepared in present study.	45
Table (4)	Molecular weight results for the starting polyether raw material Jeffamine M-2070	59
Table (5)	Molecular weight distribution of dispersants (R 1 – R 5).	60
Table (6)	Molecular weight distribution of dispersants (C 1 – C 5).	62
Table (7)	Molecular weight distribution of dispersants (A 1 – A 5).	64
Table (8)	Particle size distribution before and after stability test of prepared cyan 15:3 inkjet inks.	66
Table (9)	Particle size distribution before and after stability test of prepared cyan 15:3 inkjet inks.	71
Table (10)	Color strength and gloss measurement of dried cyan 15:3 ink film before and after stability.	76
Table (11)	Color strength and gloss measurement of dried black 7 ink film before and after stability.	78

LIST OF SCHEMES

Scheme No.	Title of scheme	Page
Scheme (1)	Polyvinyl pyrrolidone dispersants	15
Scheme (2)	Structure of the graft polymeric dispersant	16
Scheme (3)	Polymeric surfactants prepared	17
Scheme (4)	Schematic representation of SiO ₂ particle dispersion by AB diblock, ABA triblock and comb copolymer dispersants	18
Scheme (5)	Reaction of ATRP of poly(BA)-b-poly(HEMA)-poly(MMA) and post modification	19
Scheme (6)	Mannich reaction involving resorcinol, formaldehyde and a primary amine	20
Scheme (7)	Side reaction during acid catalyzed Mannich Bases	21
Scheme (8)	Resorcinol pyrrole-2-carboxaldehyde resin	22
Scheme (9)	Calix[4]resorcinarene adduct synthesis	23
Scheme (10)	Resorcinol-formaldehyde resin	24
Scheme (11)	Acetone-resorcinol-formaldehyde resin	25
Scheme (12)	Octa-O-methoxy resorcin [4] arene - Amberlite XAD-4 chelating resin	26
Scheme (13)	Synthesis of cyclohexanone-formaldehyde resin	27
Scheme (14)	Formation of cyclohexanone-formaldehyde	28

	resin in a first step	
Scheme (15)	Formation of final epoxy resin via reaction of (1) with epichlorohydrin	28
Scheme (16)	Preparation of UV curable cyclohexanone-formaldehyde resin	29
Scheme (17)	Synthetic route of methylolated cyclohexanone-formaldehyde resin and their glass reinforcement	30
Scheme (18)	Schematic impression of cyclohexanone-formaldehyde resin	31
Scheme (19)	Mechanism for incorporation of cyclohexanone-formaldehyde resin into the alkyd network	31
Scheme (20)	Synthesis of an azo dye	33
Scheme (21)	Polymerization of the dye prepared with o-aminobenzoic acid using formaldehyde	34
Scheme (22)	Polymerization of diazotized-sulphanilic acid dye with o-aminobenzoic acid using formaldehyde as linker	35
Scheme (23)	Nickel surface coating using p-aminobenzoic acid-formaldehyde resin	35
Scheme (24)	Possible structures of p-aminobenzoic acid-cyclohexanone-formaldehyde resin	36
Scheme (25)	Curing of epoxy resin using hardener	37

Scheme (26)	Synthesis of dispersants (R1-R5).	47
Scheme (27)	Reddish xanthene side product during synthesis of resorcinol-aldehyde condensates	48
Scheme (28)	Synthesis of dispersants (C1-C5)	49
Scheme (29)	Side reaction of cyclohexanone forming tri-substituted adducts	50
Scheme (30)	Dibenzylidenecyclohexanone side product	51
Scheme (31)	Synthesis of dispersants (A1-A5).	52
Scheme (32)	Side products of p-Aminobenzoic acid reactions	53