SYNTHESIS OF MONOAZO PIGMENTS BASED ON β-NAPHTHOL AND ACETOACETANILIDES AND THEIR APPLICATIONS

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DECLARATION

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any other University or Institution. The information derived from the published work of others has been duly acknowledged in the text by means of reference.

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CERTIFICATION

This thesis entitled “Synthesis of Monoazo Pigemnts based on β-naphthol and acetoacetanilides and their application” by Yusuf Yakubu meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University and is approved for its contribution to Scientific Knowledge and literary presentation.

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DEDICATION

This work is dedicated to Almighty Allah, the Omniscient the Beneficent, the Merciful.

ACKNOWLEDGEMENT

My profound gratitude goes to my supervisors: Professor P.O. Nkeonye and Dr. S.S Achi who took time to meticulously supervise this research work. In fact their critical observations, moderations, corrections and patience saw to the successful completion of this work.

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Last but not the least is Mike Gagas, the multitalented computer operator who painstakingly typed the thesis.

ABSTRACT

Aniline, m-toluidine, o-nitroaniline, 4-nitroaniline and 2,4-dinitroaniline were used to synthesize twelve pigments based on β-naphthol, acetoacetanilide and acetoacet-2,5-dichloroaniline coupling components using the general principle of diazotisation and coupling. The amount of diazo components and coupling components used for synthesis is directly proportional to the yield of the resultant pigment but has no effect on the pigments properties. Most of the synthesized pigments with the exception of pigment derived from 2,4-dinitroaniline and β-naphthol did not recrystallise fully in glacial acetic acid and none at all recrystallised from xylene, benzene or toluene. However, a few of the pigments partially recrystallised in 2-ethoxyethanol.

Visible absorption measurements of the pigments were determined. The results indicated that among the pigments (A, D, G, J) synthesized using β-naphthol, pigment A had the lowest λ_{max} (449.3nm) while J absorbed maximally at λ_{max} (498.5nm). For pigments B, E, H, K and M synthesized using Acetoacetanilide, the highest λ_{max} was indicated by H λ_{max} (478.5nm) and M gave the lowest λ_{max}(439.6nm).

The use of Acetoacet-2,5-dichloroaniline as coupling agent for pigments C, F, I indicated similar pattern of absorbance compared to those synthesized from β-naphthol and acetoacetanilide with F having the lowest λ_{max}(432.5nm).

The pigments were applied to cotton, polyester, wool, cotton/polyester blend and paper, after which their fastness properties were investigated.

It was found that the presence of an electron donating group ($-NH_2$,$-CH_3$ etc) positioned on the ortho, meta, or para position of the electron withdrawing ($-NO_2$) group on the arylamine imparted reasonably on the resonance of the pigments. The analysis of the results indicated that pigments synthesized based on β-naphthol are better applied on cotton, polyester and cotton/polyester blend while the acetoacetarylide-based pigments are more useful on wool and paper. In virtually all cases, the pad-bake method of application gave better result than the resin-bond-bake method.

On general account the pigments had good fastness to washing while light fastness was only moderate.

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CHAPTER ONE

INTRODUCTION

1.1 Pigments and Pigment Properties:

Pigments are crystalline colouring substances manufactured in finely divided form. They are generally distinguished from dyes as colouring materials on the basis of their solubility characteristics. Christie (1993).

The principal use of dyes is in the colouration of textile fibres. Textile dyes are applied from aqueous solution and are therefore required to have a degree of solubility in water, or be capable of conversion to a water-soluble form as with vat dyes. Pigments are used mainly in the colouration of paints, printing inks, plastics, and to a certain extent in the coloration of textiles, ceramics, paper and cosmetics.

In contrast to dyes, pigments are highly insoluble colouring materials, which are incorporated into an application medium by dispersion, and they remain as discrete solid particles held mechanically within a polymeric matrix. Pigments are thus required to resist dissolving in solvents, which they may contact during application to minimize problems such as “bleeding” and migration.

During application, the optical properties of the pigment, its hue and opacity are critical factors. Apart from imparting opacity, high transparency may be essential, for example in inks used in multicolour printing processes, where optical effects of the first colour printed must not be obscured by subsequent printed colours.

Other paramount pigment properties include: colour strength, fastness to solvents, oil absorption, fastness to chemicals such as alkalis, acids and other extraneous reagents such as bleaching agents. In terms of colour strength, the lighter the better, especially in the case of printing inks.

Fastness To Solvents

An ideal pigment should be insoluble in all media. Generally this condition is not fulfilled and as such some loss of pigment will inevitably result. Consequently, there will be a loss in colour strength and a reduction in fastness to light in use.

Oil Absorption

The rheological properties of inks and paints depend on oil absorption of the pigments from which they are derived.

Fastness To Chemicals

Fastness to chemicals such as acids and alkalis etc. depends on the environment in which the pigment is being used. The fastness properties of a pigment are generally dependent on its chemical constitution, and the size of the molecule is of great importance. Amongst other considerations, a sufficiently high molecular weight is necessary to ensure resistance to sublimation and an acceptable degree of insolubility in dispersion media.

Fastness To Light

It is of great significance that pigments should have very good light fastness when exposed for a long period to broad daylight and ultra-violet radiations.

Fastness To Heat

Pigments to be used for baking elements and moulded plastics should have good fastness to heat. These pigments are also expected to have good fastness to sublimation and high melting points.

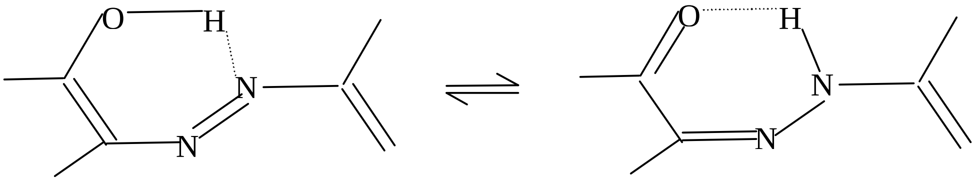
Pigments are conveniently classified as either organic or inorganic. The main focus of this work, however, is on monoazo pigments, which are purely organic.

Organic pigments generally provide higher intensity and brightness of colour than inorganic pigments. This is in most cases attributed to the $\pi - \pi*$ electronic transitions associated with the extensively conjugated aromatic systems of colourants. Organic pigments are unable to provide the degree of opacity offered by most inorganic pigments because of the lower refractive index associated with organic crystals. However, the combination of high colour strength and brightness with high transparency means that organic pigments are especially suited to mainly printed ink applications. The largest tonnage inorganic pigments are rutile titanium dioxide (TiO_2), C.I Pigment White 6, and carbon black, C.I Pigment Black 6&7, while the single most important organic pigment is copper phthalocyanine (CuPc), C.I Pigment Blue 15. Christie (1993).

1.2 Azo Pigments

Azo pigments both numerically and in terms of tonnage produced, dominate the yellow, orange and red shade areas in the range of commercial organic pigments.

Azo colourants are generally described structurally as components containing one or more azo group(s) (-N=N-) linked to two carbon atoms which may not always be part of the aromatic ring systems. Most azo compounds contain a hydroxyl group at a position ortho to the azo group. This is due to the possibility of tautomerism between hydroxyazo and ketohydrazone forms.



Hydroxyazo – ketohydrazone tautomerism

The range of yellow azo pigments is dominated by the azo acetoacetanilide of both mono-azo and disazo types. Monoazo yellow pigments, traditionally known as Hansa Yellows have a wide variety. In general, they are characterized by good light fastness but rather poor resistance towards organic solvents. For this reason, they tend to be used in applications such as water-based decorative paints where the deficiency is not critical.

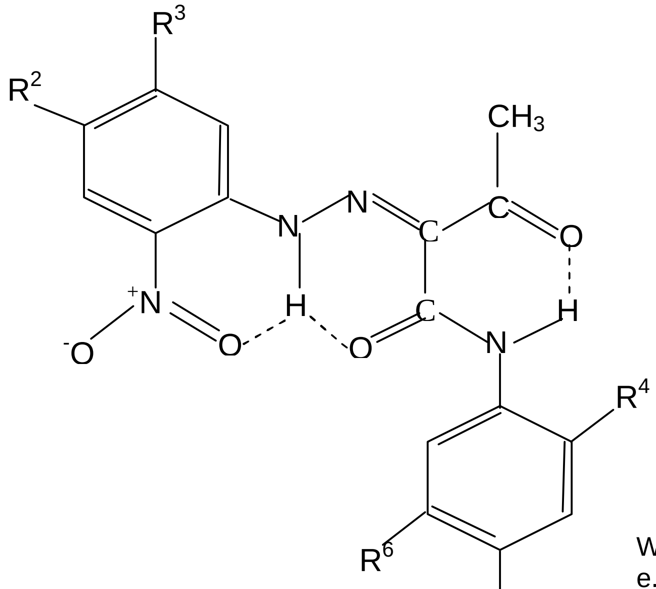
The good light fastness of monoazo pigments may be attributed to the high stability, which results from the extensive intramolecular H-bonding in 6-membered, rings in which the nitro and amide groups participate.The poor fastness to organic solvents may be accounted for in part by the observation that the intermolecular interactions involve principally only Van der Waals' force. Although, in the case of some compounds weak intermolecular

H-bonding has been tentatively suggested.

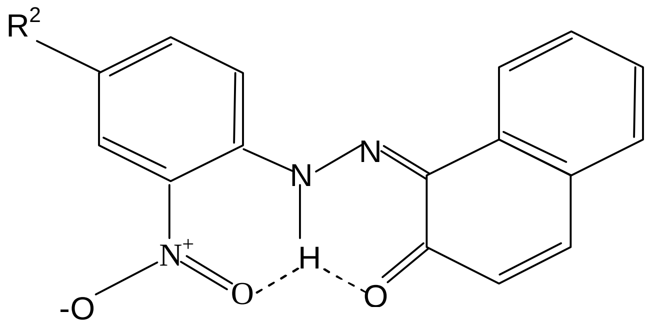
C.I Pigment Yellow 74 is a particularly important member of the monoazo acetoacetanilide series in view of its especially high colour intensity. It has been demonstrated that the enhancement in colour strength is due to the presence of the nitro group para to the azo (hydrazone) linkage, rather than in the ortho position as is the case with most other members of the series.

C.I Pigment Yellow 97 is also a product of some importance offering excellent colour strength and light fastness and significantly improved solvent resistance compared with the rest of the Hansa Yellow series. The enhanced properties of this pigment are attributed to its higher molecular size and polarity, with the sulphonamide group playing an important role. Christie (1993).

Structure of monoazoacetoacetanilides



Where R^2,R^3etc. are substituents e.g CH_3, Cl, H etc.



Structure of azo naphthols

1.3 Synthesis of monoazoacetoacetanilides

Monoazoacetoacetanilides just like all other classical azo pigments are synthesized by the standard two-stage synthetic route to azo colourants, namely, diazotisation of primary aromatic amines and coupling of the diazonium salt which is formed with the appropriate coupling component.

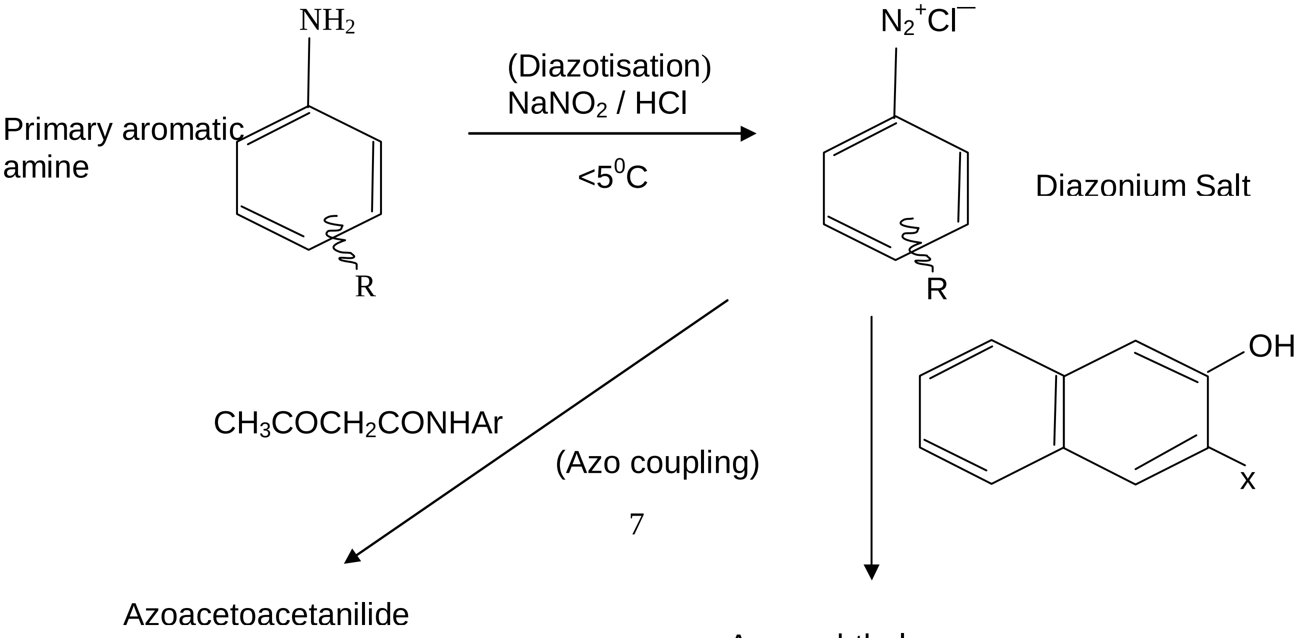
Principle

Primary aromatic amines generally referred to as diazo components, react smoothly with sodium nitrite under aqueous acid conditions to form a diazonium salt. Diazotization reaction is carried out at low temperatures (generally less than 5^0C) due to the inherent instability of diazonium salts, and the solutions of the diazonium salts, which are formed, are used in-situ without isolation.

The azo coupling reaction is an electrophilic substitution reaction in which the diazonium cation acts as the electrophile. Common coupling components used in the synthesis of azo pigments include phenols especially 2-naphthol and its derivatives, heterocyclic derivatives, notably 3-methyl-1-aryl-5-pyrazolones and reactive methylene compounds notably the acetoacetanilides. These diazo and coupling components shall be used in this work. The azo coupling reaction is carried out in water as the reaction solvent. The need for careful control of pH is an important feature of the reaction. In general, naphthols require alkaline conditions for coupling while acetoacetanilides and pyrazolones couple under weakly acidic conditions.

Below is the general route to the synthesis of monoazo pigments.

1.3.1 Synthesis of monoazo pigments



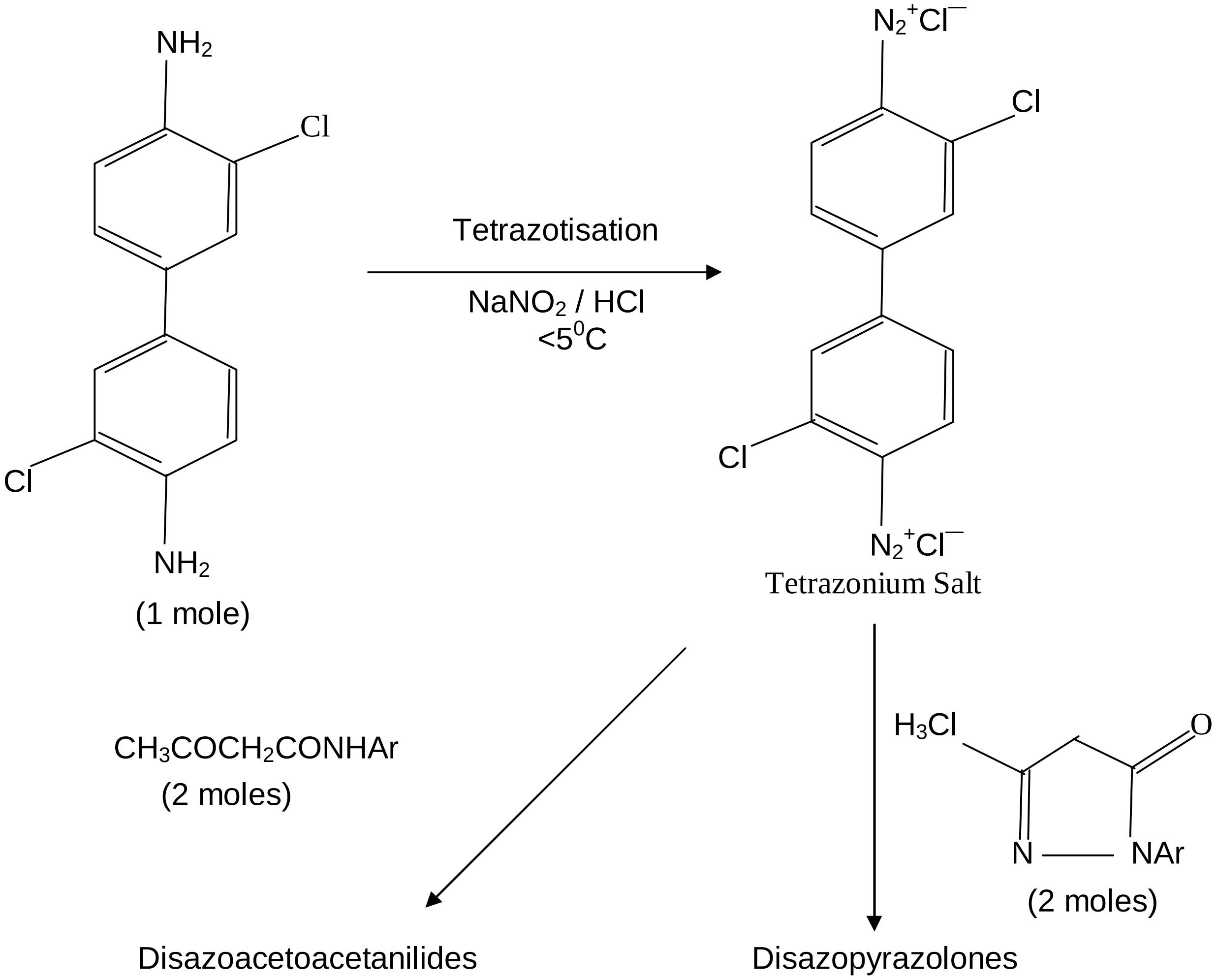
Monoazo pigments provide bright intense colours at relatively low cost but, in general, they lack the exceptional fastness towards light, weathering, heat and particularly solvents, which are required in applications such as for automotive paints. Disazo pigments are prepared by tetrazotization (bisdiazotisation) of the appropriate diamine, most commonly 3, 3 Christie (1993) -dichlorobenzidine and reaction with two equivalents of the coupling component. Metal salt azo pigments are prepared by traditional diazotization/coupling processes to form a sodium salt of an azo dyestuff. This is then treated with a solution of an appropriate salt of the divalent metal, which displaces the sodium.

The dominant positon of azo pigments in the range of organic pigments owes much to the simplicity and versatility of the synthetic sequence, which uses expensive commodity intermediates and water as the reaction medium.

The reactions are low in energy requirements and, in addition, provided that careful control of the reaction condition is maintained, the pigments may be prepared directly in high yield and in the optimum physical form. Because of its prime importance, the synthesis of azo colourants is one of the most extensively documented topics in colour chemistry.

Below is the route to the synthesis of disazo pigments.

1.3.2 Synthesis of Disazo pigments



1.4 Objectives of the study

The objectives of the study are:

1. To synthesize monoazo pigments from Aniline, m-toluidine, o-nitroaniline, 4-nitroaniline and 2,4-dinitroaniline as diazo components and β-naphthol, acetoacetanilide and acetoacet-2,5-dicloroaniline as coupling components.
2. To apply the synthesized pigments to cotton, polyester, wool, cotton/polyester blend and paper with a view to assessing the applicability of the pigments to the substrates mentioned.

CHAPTER TWO

LITERATURE REVIEW

2.1 Definition of Pigments

Pigments have been defined in several ways. According to Gurdeep(1990) “Pigments are insoluble powders of very fine particle size, i.e. as small as 0.01 micron, which are used in paints, plastics, rubber, textiles, inks and other materials to impart colour, opacity and other desirable properties to the product”.

Fairchild’s Dictionary of Textiles defined a pigment as “an insoluble colouring matter of fine particle size”. (Isabel, 1984).

The Textile Institute defined pigment as “a Substance in particulate form that is substantially insoluble in a medium but which can be mechanically dispersed in this medium to modify its colour and light scattering properties. (TI, 1991) However, Christie (1993) said Pigments are “highly insoluble colouring materials which are incorporated into an application medium by dispersion, and they remain as discrete solid particles held mechanically within a polymer matrix”.

The operating word insoluble, dispersion, and fine particle size seem to be common to any definition of pigment(s).

2.2 History of Pigments

Natural organic pigments derived mainly from mineral resources, have been used as colourants since prehistoric times and a few, notably iron oxides, remain of some significance today. (Lenoir, 1972).

The origins of the synthetic inorganic pigment industry may be traced to the introduction of prussian blue in the early 18th century predating the synthetic organic colorant industry by about 150 years.

The years since then have seen the development of a range of technically superior modern synthetic inorganic pigments–incorporating white pigments, by far the most important of which is titanium dioxide; black pigments – notably carbon black, and coloured pigments of a number of chemical types, including oxides (e.g. of iron and chromium), sulphides (principally of cadmium), chromates (principally of lead) and the structurally more complex ultramarines and Prussian blues. (Herbst *et al*, 1987). Synthetic organic pigments emerged towards the end of the 19th century out of the established synthetic textile dyestuff industry. (Lenoir, 1972). (Herbst *et al*, 1987). Many of the earliest organic pigments were known as “lakes”. These products were prepared from established water–soluble dyes by precipitation onto an insoluble inorganic substrate. The introduction of a range of azo pigments was a further significant early development in organic pigments. Azo pigments remain the most important commodity; yellow, orange and red organic pigments currently in use, providing bright intense colours but generally only of moderate performance in terms of fastness properties.

The discovery of copper phthalocyanine blue in 1928, (Griffiths, 1976) however, was one of the most critical events in the development of organic pigment industry. Copper phthalocyanine was the first organic pigment to offer the outstanding intensity and brightness of colour combined with an excellent range of fastness properties, comparable with many inorganic pigments.

The discovery stimulated numerous research programmes aimed at developing new types of organic pigments, which could emulate the properties of copper phthalocyanine in the yellow, orange, red and violet shade areas.

This research gained further impetus in the middle of the 20th century from the development of the automative paint industry and the growth of the plastics and synthetic fibre industries, applications that demanded high performance pigments.

Out of this research, a wide range of high performance pigments emerged; a variety of chemical types including quinacridones, tetrachloroisoindolinones, dioxazines, perylenes, perinones and a number of high grade azo pigments. In more recent years, the number of new organic pigments, which has been introduced into the market, has decreased, reflecting a transfer of research emphasis by the pigment industry away from new chemical types and towards process and product improvement.

Nevertheless, the discovery and successful commercial introduction of new products, such as the diketopyrrolopyrrole (DPP) (Ciba, 1984). pigments in the 1980s, shows that more research can still be done by the synthetic organic pigment chemist. (Ciba, 1985).

2.3 Classification of pigments

Pigments are broadly classified into two, namely inorganic and organic pigments according to their chemical nature.

2.3.1 Inorganic pigments

2.3.1.1 Titanium dioxide and other white hiding pigments

White hiding pigments, as a result of their high refractive index, are capable of conferring high opacity in applications such as paints where this feature is of critical importance, plastics, inks, fibres and cosmetics. White non-hiding pigments, or extenders are considerably lower refractive index materials and as a result play a minor role in providing opacity, but are extensively used in a variety of ways, for instance to modify the flow properties of paints and inks and to modify the mechanical properties and lower the cost of plastic materials.

The best example of white hiding pigments is titanium dioxide and examples of non-hiding pigments include calcium carbonate, barium sulphate, and silicates of magnesium, calcium, and aluminium.

Titanium dioxide (Titanium IV oxide), C.I. Pigment White 6, was first introduced in the 1920s (Christie, 1993) and grew rapidly in importance, to emerge as by far the most important white hiding pigment for a variety of applications, including paints, plastics, printing inks, rubber, paper, synthetic fibres, ceramics and cosmetics .The product owes its dominant position to its ability to provide a high degree of opacity with minimum light absorption and its excellent durability and non-toxicity. (Ferguson, 1983).

Titanium dioxide exists in three polymorphic forms: rutile, anatase and brookite. (A material exhibits polymorphism if it is capable of existing in various forms with identical chemical composition but different crystal lattice structures). Both rutile and anatase forms of titanium dioxide are produced commercially. However, the rutile form is considerably more important, principally because it is inherently more opaque as a result of its high refractive index.

Brookite, the rarest of the three forms, is not useful commercially.

Manufacture Of TiO_2

Two processes are used in the manufacture of titanium dioxide pigments: the "Sulphate" process, and the "chloride" process.

2.3.1.1.1 Sulphate process

The major portion of the world's production of titanium dioxide pigments is by the sulphate process, the raw material for which is ilmenite. (Christie, 1993).

The ground ore (crude ilmenite) which contains titanium dioxide with substantial quantities of oxides of iron, is first digested with sulphuric acid, giving a solution containing the sulphates of Ti (IV), Fe (III) and Fe (II). Treatment of this solution with iron metal then effects reduction of the Fe (III) ensuring that the iron in solution is excessively in the oxidation state Fe (II).

The solution at this stage is then concentrated depositing crystal of $FeSO_4. 7H_2O$ (Copperas), (Christie, 1993) a major by-product of the process, which is removed by filtration. Subsequently, the solution is boiled, leading to a precipitate of hydrated titanium dioxide as a result of hydrolysis of the aqueous titanium (IV) sulphate.

The aqueous chemistry of Ti (IV) is now suggested to involve a number of hydroxocomplexes derived formally from the simple hexaaqua ion (1) in a series of equilibria (1), (2) and (3)

$$\underset{(1)}{[Ti\,(H_2O)_6]^{4+}} + H_2O \leftrightarrows \underset{(2)}{[Ti\,(H_2O)_5OH]^{3+}} + H_3O^{3+} \qquad (1)$$

$$\underset{(2)}{[Ti\,(H_2O)_5OH]^{3+}} + H_2O \leftrightarrows \underset{(3)}{[Ti\,(H_2O)_4(OH)_2]^{2+}} + H_3O^{3+} \qquad (2)$$

$$\underset{(3)}{[Ti\,(H_2O)_4(OH)_2]^{2+}} + H_2O \leftrightarrows \underset{(4)}{[Ti\,(H_2O)_3(OH)_3]^{+}} + H_3O^{+} \ (2)$$

2.3.1.1.2 The “chloride” process

This is a more modern process than the sulphate process. In this process, the rutile titanium dioxide ore is initally treated with chlorine in the presence of coke as a reducing medium at 800 – 1000^{0}C to form titanium chloride. The reaction is as represented below.

$$TiO_2 + C + 2Cl_4 \longrightarrow TiCl_4 + CO_2$$

After Purification by distillation, the tetrachloride is subjected to gas–phase oxidation at 1500^{0}C with air or oxygen to yield a high purity, fine particle size rutile titanium dioxide pigment represented by the equation below.

$$Ti\ Cl_4 + O_2 \longrightarrow Ti\ O_2 + 2Cl_{2.}$$

The “chloride” process offers certain inherent advantages over the “sulphate” route. These include suitability for continuous operation, excellent control of pigment properties and fewer by-products, which in the case of “sulphate” process can lead to disposal problems. (Christie 1993).

2.3.1.2 Iron oxide pigments.

These are by far the most important coloured inorganic pigments. They provide shades ranging from yellow and red to brown and black.

Iron oxide pigments, though are cheap (low cost) exhibit excellent durability. Their major deficiency however, is their low intensity and brightness of colour. Both natural and synthetic iron oxide pigments are produced.

Micaceous iron oxide is a natural pigment used in metal – protective coatings. It has a flake – like particle structure, which resemble that of mica. The particle laminate in the paint film, forming a reflective surface which reduces radiation degradation of the film, and providing barrier to moisture as an aid to corrosion protection. Other examples of natural iron oxide pigments include yellow ochre, red haematite and burnt sienna. Synthetic iron oxides offer the advantages of chemical purity and improved control of physical form over their natural counterparts.

2.3.1.3 Coloured sulphides and sulphoselenides

The most important example of this class of pigments is the cadmium sulphides and sulphoselenides. These pigments provide a range of moderately intense colours ranging from yellows through oranges and red to maroons. They are of particular importance in the coloration of thermoplastics, especially high melting point polymers, which are processed at high temperature, because of their outstanding heat stability.

Cadmium sulphides are prepared by aqueous precipitation processes using suitable water soluble sources of Cd^{2+} and S^{2-} as represented by the equation below.

$$CdSO_4 + Na_2S \longrightarrow CdS + Na_2SO_4$$

The use of cadmium – containing pigments is restricted to a considerable extent on the grounds of potential toxicity, by legislation in certain cases. (Cadmium,1992).

2.3.1.4 Chromates

Lead chromate pigments provide a range of hues, from greenish-yellow through orange to yellowish – red. They offer good fastness properties, a remarkably high brightness or purity of colour for inorganic pigments and high opacity at relatively low cost. Lead chromate pigments produced in the early part of the 20th century showed a tendency to darken on exposure to light, an effect which has been attributed to reduction to lead chromite. In addition, in areas of high industrial atmospheric pollution, lead chromate tended to darken as a result of the formation of lead sulphide from attack by hydrogen sulphide. These deficiencies have been overcome by the use of surface treatment with oxides, e.g. Silica, and the modern range of pigments now offer excellent durability. (Cowley, 1986).

2.3.1.5 Ultramarines

Ultramarine Blue (C.I. Pigment Blue 29) is the best – known and by far the most important of this small group of pigments. Other examples are Violet (C.I. Pigment Violet 15) and pink pigments.

Ultramarine Blue offers excellent fastness to light and heat at moderate cost and it is applied mostly to plastics.

Although capable of providing brilliant reddish – blue colours in application, ultramarine blue suffers from poor tinctorial strength.

As an example, the pigment has less than one-tenth of the colour intensity of copper phthalocyanine blue, the most important organic blue pigment. A further deficiency of the pigment is its poor resistance towards acids. (Clark *et al,* 1983).

2.3.1.6 **Prussian blue**

Prussian blue (C.I. Pigment Blue 27), known also by a range of names such as iron blue and milori blue, is the longest established of all synthetic colourants and retain moderate importance as a low cost blue pigment. Prussian blue, on the basis of single crystal X-ray diffraction studies, is best represented as the hydrated iron (III) hexacyanoferrate (II), $Fe_4 [Fe (CN)_6]_3 .nH_2O$. However, when precipitated in the fine particle size essential for its use as a pigment, significant and variable amounts of potassium or ammonium ions are incorporated into the product by surface absorption or occlusion. In addition the commercial products may contain indefinite amounts of water and they can exhibit variable stoichiometry and a degree of structural disorder. (Ganguli et al, 1983).

2.3.1.7 **Carbon black**

Carbon black (C.I. Pigment Black 6 and 7) dominate the market for black pigments, providing an outstanding range of properties at low cost and finding wide range of applications.

The most important outlet for carbon black pigments, however, is in rubber. And apart from providing the colour, they serve as reinforcing agents.

Although carbon black is most of the time classified as an inorganic pigment, and the present literature has chosen to follow tradition in this respect, there is enough justification for classifying the product amongst the high grade organic pigments; for example, the nature of the bonding in carbon black and the mechanism of its formation involve the principles of organic chemistry, whilst many of its properties, especially the high absorption coefficient, are arguably more closely related to those of organic than inorganic pigments. (Abrahamson, 1977). The structure of the two crystalline forms of carbon, diamond and graphite, are well established. Graphite consists of large sheets of carbon atoms in 6 – membered rings and an associated system of extensively delocalized π - electrons. The C–C bond distance (0.142nm) is comparable to that in benzene (0.139nm) and thus typical of aromatic systems. The sheets are layered parallel in ordered positions, every other layer having the same orientation.

Carbon blacks have been described as having an imperfect graphite structure in which the layers are parallel but further apart and arranged irregularly.

Carbon blacks are manufactured from hydrocarbon feedstock by partial combustion or thermal decomposition in the gas phase at high temperatures. The products are usually classified according to the manufacturing method used as furnace, channel, lamp, thermal or acetylene blacks.

A continuous furnace black process, which involves the treatment of viscous residual oil hydrocarbons, containing a high proportion of aromatics, with a restricted amount of air at temperatures of 1400 – 1600^0C, today dominates world production.

Titanium dioxide and carbon black are the two largest tonnages inorganic pigments manufactured currently. (Abrahamson, 1977).

2.3.2 Organic pigments

Organic pigments generally provide higher intensity and brightness of colour than inorganic pigments. These colours are in most cases attributed to the $\pi - \pi*$ electronic transitions associated with the extensively conjugated aromatic systems of the colourant. (Griffiths, 1984)

Organic pigments are unable to provide the degree of opacity offered by most inorganic pigments because of the lower refractive index associated with organic crystals. However, the combination of high colour strength and brightness with high transparency means that organic pigments are especially suited for many printing inks applications.

Since organic molecules will usually tend to exhibit some tendency to dissolve in organic solvents, organic pigments frequently contain structural features designed to enhance solvent-fastness.

Increasing molecular size often leads to improved solvent resistance, but need not necessarily enhance other fastness properties. The amide (–NHCO–)

group is commonly encountered in organic pigments. Its presence in an organic molecule frequently enhances fastness to solvents, light and heat. This may be attributed to the ability of the group to participate in strong dipolar interactions and in hydrogen-bonding, both intramolecular and intermolecular. The incorporation of halogen substituents and metal ion is often found to have a beneficial effect on fastness properties. In addition, halogen substituents also provide desirable shade modification. (Griffiths, 1984).

The wide variety of chemical types encountered in organic pigments complicates considerable attempts at systematic classification.

A system of chemical classification used here is based on that used by (Rys *et al,* 1972) in which pigments of different types but containing common structural features are collected together. On this basis, the products have been classified as azo, metal complex, carbonyl azomethine or triarylmethane pigments. (Rys *et al*, 1972), (Gurdeep, 1990).

2.3.2.1 Azo pigments

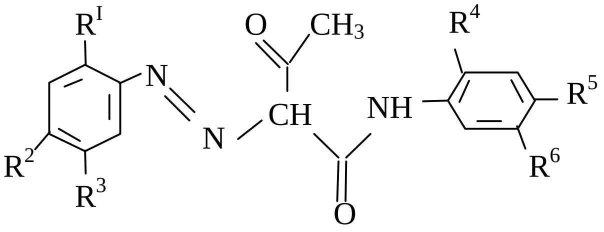
Azo pigments, both numerically and in terms of tonnage produced, dominate the yellow, orange and red shade areas in the range of commercial organic pigments. Azo colourants are generally described structurally as compounds containing one or more azo (-N=N-) groups linked to two carbon atoms, which are usually, though not always, part of aromatic ring systems. (Christie, 1993).

Azo dyes and pigments form the largest group of all synthetic colourants. The chromophoric system of these pigments is the azo group, (-N=N-), in association with one or more aromatic systems. There may be more than one azo group present in the pigment molecule and thus depending on the number of azo groups in the pigment molecule one speaks of monoazo, disazo, trisazo, tetrakis azo and polyazo pigments or dyes. (Gurdeep, 1990).

Azo pigments have been categorized as either classical azo pigments,which are long established products offering good colouristic properties, but moderate performance in terms of fastness properties at relatively low cost, or high grade azo pigments which provide superior performance suitable for automotive paint and other demanding applications, generally at higher cost. (Christie, 1993).

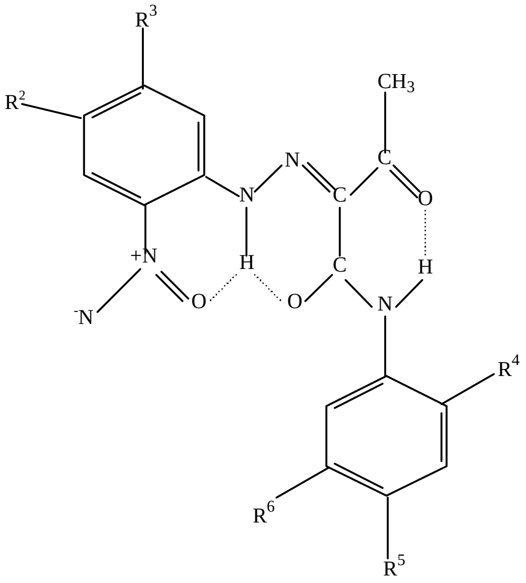
2.3.2.1.1 Classical azo pigments

The range of yellow azo pigments is dominated by the azoacetoacetanilides, of both monoazo and disazo types. Below is a typical structure of an azoacetoacetarilide



Compound	C.I Pigment yellow	R_1	R_2	R_3	R_4	R_5	R_6
	1	NO_2	CH_3	H	H	H	H
	2	NO2	Cl	H	Cl	H	H
	65	NO_2	OCH_3	H	OCH_3	H	H
	74	OCH_3	NO_2	H	OCH_3	H	H

The molecules exist in the ketohydrazone tautomeric form and adopt the essentially planar configuration shown in the structure below.



The structure of monoazoacetoacetanilides

The good light fastness of the products may be attributed to the high stability, which results from the extensive intramolecular H-bonding in 6-membered rings, in which the nitro and amide groups participate. The poor fastness to organic solvents may be accounted for in part by the observation that the intermolecular interactions involve principally only vander Waal's forces.

C.I Pigment Yellow 74 is a particularly important member of the monoazoacetoacetanilide series in view of its especially high colour intensity. It has been demonstrated that the enhancement in colour strength is due to the presence of the nitro (-NO_2) group para to the azo (hydroazone) linkage rather than in the ortho position as is the case with most members of the series.

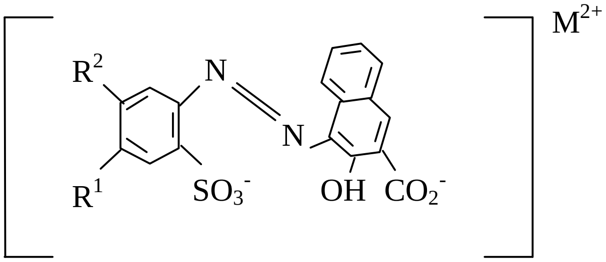
Disazoacetoacetanilides are a group of classical azo pigments, which contain the most important of all the yellow organic pigments.

These pigments are also commonly referred to as Diarylide Yellows or Benzidine Yellows. These products exhibit higher colour strength and transparency than the monoazo pigments, and better solvent fastness attributable to the larger molecular size. The properties of disazoacetoacetanilide pigments are particularly well suited to printing ink applications. (Whitaker, 1988).

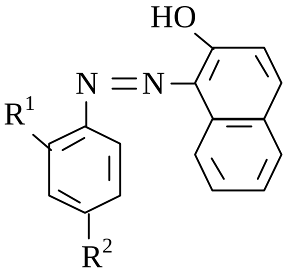
The most important classical orange organic pigments are the disazopyrazolones. These products are structurally similar to the disazoacetoacetanilides, and they exhibit very similar technical properties which accounts for their importance particularly in printing inks pigments

The most important of the classical red azo pigments are metal salts, derived from azo dyestuffs containing – SO_3-Na^+ or – CO_2 – Na^+ groups by replacement of the Na^+ ions with divalent metal ions, notably Ca^{2+} , Ba^{2+} and Mn^{2+}. These products have evolved from a number of “lake” pigments, now largely obsolete, which were essentially anionic azo dyestuffs precipitated on to inorganic substrates such as alumina or barium sulphate. The metal salt azo pigments currently in use commonly referred to as “toners”, no longer contain the inorganic substrates as an integral constituent.

Below are further examples of yellow, orange and red classical pigments



where R^1, R^2, are CH_3, Cl and M is Ba for CI Pigment Yellow 48;

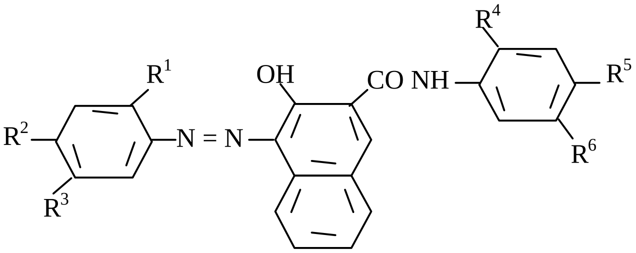


R^1, R^2 are NO_2, NO_2, for C.I Pigment Orange 5 and NO_2, CH_3 for C.I Pigment Red 3, respectively. (Harris *et al*, 1984).

A number of metal salt azo pigments are commercially significant products providing good fastness to light and solvents in the yellow shade area. These include the azoacetoacetanilide derivative, C.I Pigment Yellow 61 and azopyrazolone derivatives, C.I Pigment Yellow 183 and C.I Pigment Yellow 191 respectively.

2.3.3 Classical monoazo pigments

These have the general formula:

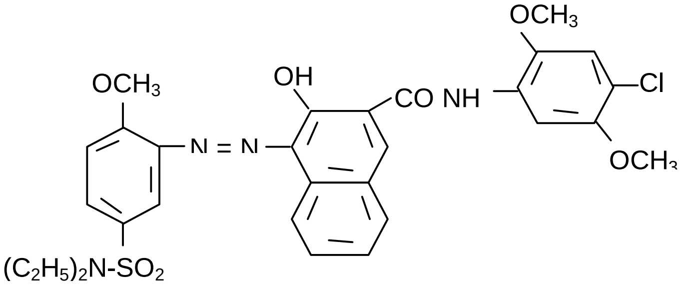


Quoted from the Colour Index, (Colour Index, 1982) for example are:

C. I	Pigment		C.I	R_1	R_2	R_3	R_4	R_5	R_6
	Red	2	12310	Cl	H	Cl	H	H	H
	Red	7	12420	CH_3	Cl	H	CH_3	Cl	H
	Red	8	12420	CH_3	H	NO_2	H	Cl	H

2.3.4 Pigments in which the diazo component is a sulphonyl compound

A typical example of pigment in this class is C.I Pigment Red 5 (C.I 12490)



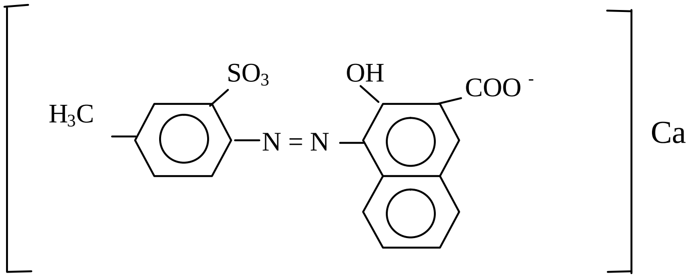
This pigment is noted for its excellent light fastness in pale tint and its good resistance to solvents. It is sometimes used in plastics owing to its low migration.

In general, pigments of this class owe their good fastness properties towards oil and alkalis to the carboxyamide function of their coupling components. They are, therefore, suitable for printing inks and viscose rayon, but their relatively high price is often an obstacle to their use in oil paints. Many of them are very fast to light and sufficiently resistant to trichloroethylene to allow their use in textile printing. Their excellent chemical resistance makes them especially useful in inks for the packaging industry (packages for food, soap, detergents, fertilizers, pharmaceuticals and chemicals are typical examples).

Other major uses for these pigments are in interior emulsion (latex paints, floor coverings and paper coatings). Emulsion paints for indoor application over alkaline substrates are commonly pigmented with the alkali-resistant red pigments. Paper coatings (primarily for packaging) and floor coverings also depend on the good to excellent chemical resistance of these pigments.

2.3.5 **Lakes and toners of 2-hydroxy-3 naphthoic acid**

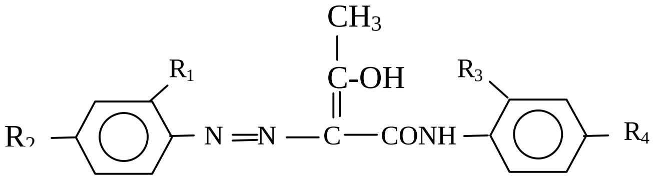
This class, which provides about one-quarter of all commercial red pigments resembles the metallized pigments derived from β-naphthol. The oldest representative of this family, C.I Pigment Red 57 (CI 15850), has the formula indicated below.



Resination of this pigment increases transparency and gives a more bluish shade in tint, without diminishing the colour strength. The most important application of these pigments is in printing inks where they are used in all fields of printing inks applications. Many of these pigments having sufficiently good dispersion properties can be used in rubber where the non-resinated types are usually employed. Various types of Ca, and Sr Reds 52 and 57 are used in low volume in plastics, their usage being limited by their somewhat deficient heat stability. (Lenoir, 1960).

2.3.6 Acetoacetarylide monoazo pigments

The common methods of improving the fastness properties by increasing the molecular size of the pigment can be applied to those pigments with azo acetoacetarylide structures. The colour of these pigments range from greenish-yellow to orange. Originally introduced as Hansa, they correspond to the general formula



where R_1, R_2 is a nitro, methyl, methoxy or chlorine group. Examples of these types of pigments, which contain at least one nitro group, are indicated below.

C.I Pigment		CI	R_1	R_2	R_3	R_4
Yellow 1	1	1680	CH_3	NO_2	H	H
Yellow	2	11730	Cl	NO_2	CH_3	CH_3
Yellow	4	11665	NO_2	H	H	H

The most important in the Hansa yellow series is the original G, C.I Pigment Yellow 1 (CI 11680), often referred to as Hansa yellow or Toluidine yellow. The monoazo yellows are the most important organic yellow pigments for the paint industry. Due to their excellent alkali resistance, they are widely used in all aqueous paint systems. Other advantages over their inorganic counterparts, the chrome yellows, are no darkening when exposed to hydrogen sulphide, up to five times greater tinting strength, a lead-free composition which makes them very suitable in paints for children's toys, and an excellent bright yellow line with a high chroma. (Achi ,1985).

All these properties make them most valuable for any kind of trade-sale paint or do-it-yourself paint job. Their use in industrial paint is somewhat limited since greater amount of titanium dioxide must be added to achieve good hiding power.

Precautions must be taken in solvent system paints when using monoazo pigments because of their bleeding characteristics. The same care should be taken when using them in baking enamels, where severe blooming or sublimation is a problem.

Bleeding and cracking in many plastic materials make the Hansa yellows unsuitable for colouring most plastics materials. Only the rubber industry is using some Hansa types to any extent. Large amounts of C.I Pigment Yellows, 1,3,74 and 97 are currently produced in water dispersible form and are used mainly for wallpaper, leather finishes, adhesives and similar aqueous systems, as well as for the mass colouration of paper.

2.3.7 **High grade azo pigments**

The classical azo pigments provide bright intense colours at relatively low cost but, in general, they lack the exceptional fastness properties towards light, weathering, heat and solvents which are required for applications such as automotive paints. For these reasons the fastness characteristics of azo pigments have to be improved or upgraded. Consequently three approaches have proved successful in producing commercial products suitable for automotive paint and other demanding applications. (Christie, 1993).

2.3.7.1 **Azo condensation pigments**

This class of pigments, which covers a wide range of shades from yellow through red to violet and brown, were introduced by Ciba Geigy after an intensive research and development programme.

Azo condensation pigments are disazo pigments of large molecular size and excellent technical performance. A list of the most important structures is given in the pigment Handbook (Lewis, 1988).

2.3.7.2 **Benzimidazalone azo pigments**

These groups of pigments, introduced by Hoechst are either of the azoacetoacetanilide, or the azo naphthol types. They are a range of high-grade pigments containing the benzimidazolone ring system.

The high stability of these pigments towards light and heat and their excellent solvent resistance has been attributed to the extensive intermolecular H-bonding involving the benzimidazolone group. (Moser et al, 1963).

2.3.7.3 **Metal complex azo pigments**

A considerable amount of research has been carried out over the years in an attempt to exploit the potential of metal complex chemistry to provide high performance pigments, particularly of yellow and red shades to complement the shade range of copper phthalocyanines, which cannot be extended outside blues and greens. Consequently, a number of interesting products have emerged not only with the excellent light fastness but also excellent solvent resistance and thermal stability.

The improvement in solvent resistance of the metal complex compared with the free ligand may be explained by the increase in molecular size, and in some cases by molecular aggregation involving coordination with the metal ion throughout the crystal lattice. The enhancement of thermal stability may be due in part to the chelate effect. However, these researches have achieved only a limited degree of commercial success. The main reason for this is that the enhancement of the fastness properties of an organic ligand, which results from complex formation, is almost inevitably accompanied by a dulling of the colour.

This is due to a broadening of the absorption band as a result of overlap of the band due to $\pi-\pi*$ transitions of the ligand with those due to transition metal d-d transitions or ligand-metal change transfer transitions. Nevertheless, a number of metal complex pigments have achieved commercial significance. Notable among them are copper phthalocyanines, azo metal complexes, azo methine metal complexes, oxime metal complexes and isoindoline-based metal complex pigments. (Lenoir, 1972), (Gurdeep, 1990), (Nkeonye, 1982).

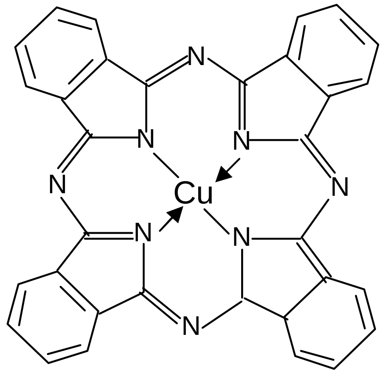
2.3.7.3.1 **Copper phthalocyanines**

The most important metal complex pigment and arguably the single most important organic pigment, is copper phthalocyanine (CuPc, C.I Pigment Blue 15).

This pigment offers exceptionally high stability to light, heat, solvent, acids and alkalis at fairly modest cost, in addition to its brilliant intense blue colour, and it finds almost universal use in the range of pigment applications. (Leznoff, 1989).

Since their discovery in 1928, the phthaloycanines have become one of the most intensively studied classes of compounds largely because of their high stability and unique molecular structure.

The molecules are planar, consisting of four isoindole units connected together by four N-atoms forming a 16-membered ring, with the central metal atom in a square planar environment.



Structure of copper phthalocyanine

It has been established that the molecule is centrosymmetric (Moser *et al,* 1963). such that the above structure should be regarded as one of a large number of resonance forms contributing to the overall molecular structure, a feature that may account for high stability. The phthalocyanines are aromatic molecules, a feature that has been attributed to the 18 π-elecrons in the perimeter of the molecule.

Copper phthalocyanine exhibits polymorphism, the most important crystal forms being the α and β forms. Both forms are of commercial importance.

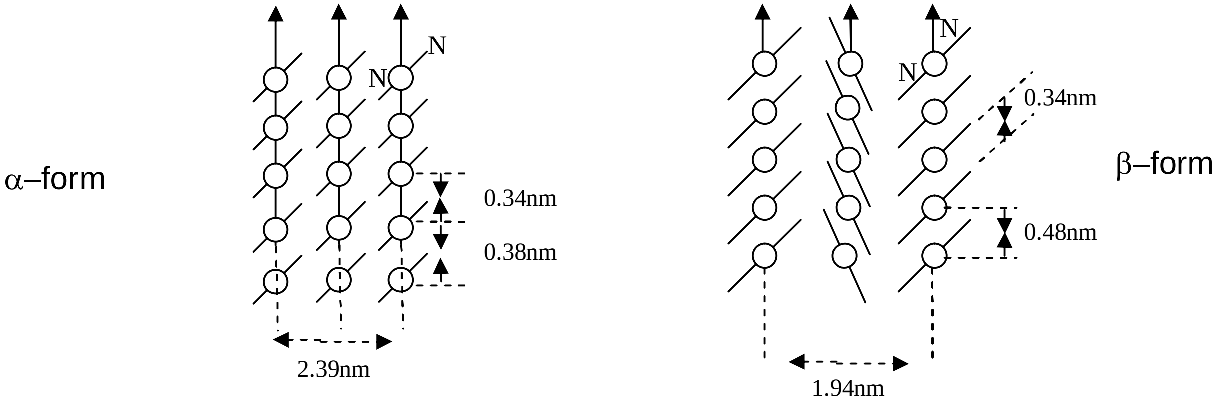
The α - form is reddish-blue whilst the β-form is the more stable form, particularly towards organic solvents, is greenish-blue.

β-Copper phthalocyanine is of particular importance as the cyan pigment for printing inks. A number of other phthalocyanines are used as pigments. The most important green organic pigments are C.I. Pigment Green 7, in which the 16 ring hydrogen atoms of the copper phthalocyanine molecules are replaced virtually completely by chlorine atoms, and C.I. Pigment Green 36, which incorporates a range of bromo and bromochloro copper phthalocyanine pigments. The shade of these pigments becomes progressively yellower with increasing bromine substitution. These phathalocyanine greens exhibit the same outstanding colouristic and technical performance as the blue pigments from which they are derived.

Synthesis of the phthalocyanine green pigments involves direct exhaustive halogenation of crude copper phthalocyanine blue with chlorine or bromine at elevated temperatures in a suitable solvent e.g. an $AlCl_3$/NaCl melt. These reactions are example of electrophilic substitution reflecting the aromatic character of the copper phthalocyanine molecule. The crude green product, which results, may be converted to pigmentary form by treatment with solvents or surfactants. These processes effect a deaggregation of the product producing a finer particle size and increased crystallinity.

Other routes to copper phthalocyarine syntheses are the phthalic anhydride route and the phthalonitrile route. Both routes produce a crude blue product, which is of far too large a particle size to be of use as a pigment. The original method for particle size reduction used was acid pasting, which involve dissolving the crude product in concentrated sulphuric acid, followed by reprecipitation with water. This gives the α form of the pigment in fine particle size form. Grinding with inorganic salts produces a mixture of α and β-CuPc, which may be converted to pigmentary β-CuPc by careful treatment with certain organic solvents.

Stacking arrangements of α and β- CuPc crystals.



Other metal complex pigments, which have limited commercial exploitation, include: azomethine metal complexes, azo metal complexes, oxime metal complexes and isoindoline-based metal complex pigments. (Leznoff, 1989).

In a related development (Gurdeep, 1990). stated that copper phthalocyanine is prepared by several methods. One method involves the heating of phthalonitrile or a related compound such as o-cyanobenzamide or phthalonitrile with cuprous salt.

Another method called urea process for the preparation of copper phthalocyanine involves heating together urea and phthalic anhydride. The yield of the method is increased by catalysts like boric acid, ammonium molybdate and ammonium phosphate. Metal-free phthalocyanine may be prepared from sodium phthalocyanine by demetallization with a strong acid. It may also be obtained directly from phthalonitrile by heating in an inert atmosphere, under pressure. It is a bright greenish pigment.

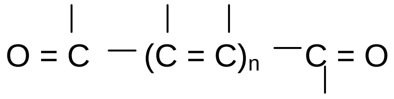
Polydichloro-copper phthalocyanine is a true green pigment. It is prepared by passing chlorine gas through a melt of copper phthalocyanine, aluminum chloride and sodium chloride at 200^0C. A number of soluble dyes have been prepared from these pigments by introducing solublising groups in the pigment.

Intensive research to obtain yellow, red and violet pigments having fastness properties similar to phthalocyanines has resulted in the production of modern high grade pigments. (Gurdeep, 1990).

2.3.7.4 **Carbonyl pigments**

Carbonyl pigments are pigments, which satisfy similar structural requirments as carbonyl dyes. That is, they contain at least two conjugated carbonyl groups. (Rys *et al,* 1972).

The structural feature of a carbonyl pigment is:



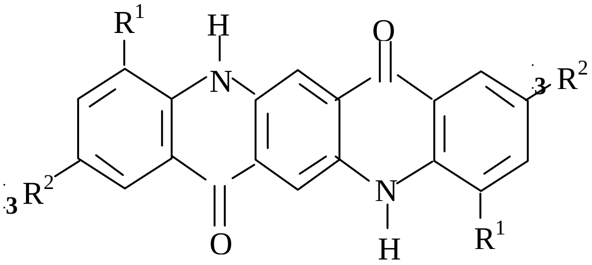
$$O = C - (C = C)_n - C = O$$

The carbonyl pigments include: Quinacridones, anthraquinones, thioindigoids, perinones, perylenes, quinophthalones, isoindolines and diketopyrrolopyrroles (DPP).

2.3.7.4.1 **Quinacridones**

Christie (1993) reported that quinacridones contribute one of the most important new chromophoric systems developed for pigment applications since the phthalocyanines.

Linear trans quinacridones were first discovered in 1935, but their potential as pigments was not realized until the late 1950s, when they were introduced commercially by Du Pont. The pigments offer outstanding fastness properties, similar to those of copper phthalocyanine, in orange, red and violet shades. A typical quinacridone pigment is C.I. Pigment Red 122.



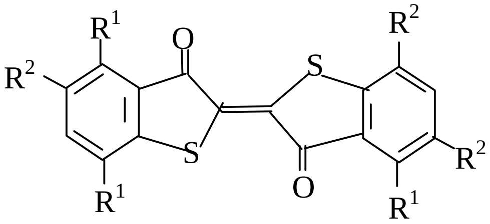
C.I Pigment Red 122

2.3.7.4.2 **Anthraquinone pigments**

The anthraquinone chromophoric grouping is second only in importance to the azo chromophore in the chemistry of synthetic textile dyestuffs, but it is of considerably less importance in pigments. This is perhaps due to the fact that the traditional role of anthraquinones in many dye application classes, which is to provide light-fast blues and greens, is more successfully adopted by the phthalocyanines in the case of pigments.

2.3.7.4.3 Thioindigoid pigments

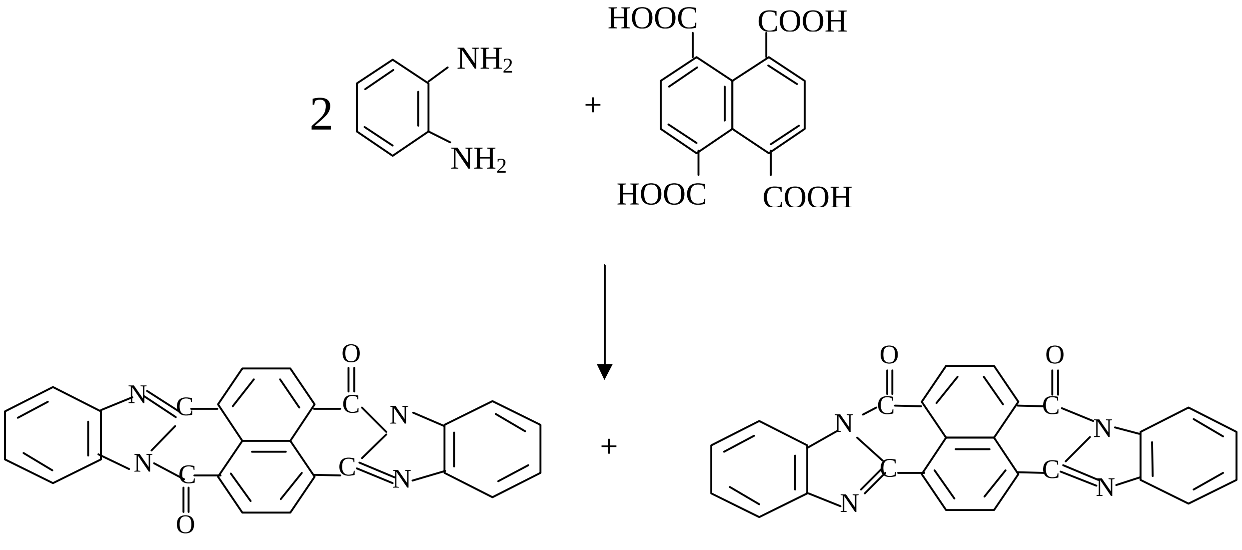
A number of thioindigoid derivatives, all of which contain halogens, are of limited importance as pigments for paints and plastics. The general formula for thioindigoid pigments is as follows:



C. I Pigment Red 68 and C.I Pigment Violet 38 with R^1, R^2 as Cl, H for Red 68 and CH$_{3,}$ Cl for violet 38 respectively are the most important commercial examples for this class of pigments.

2.3.7.4.4 Perinones

They exist in trans and cis isomeric forms, the former being especially important for plastics applications. Perinone pigments are derived from naphthalene – 1, 4, 5, 8 - tetracarboxylic acid o-phenylene (benzene-1, 2) - diamine in refluxing acetic acid. (Gurdeep, 1990), (Christie, 1987). It is a condensation process resulting in a mixture of two isomers.



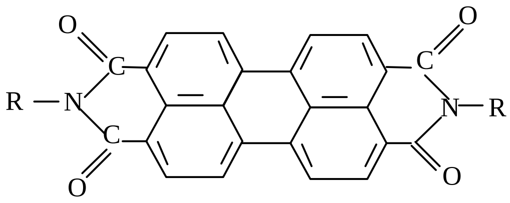
C.I Pigment Orange 43
(Trans-form)

C.I Pigment Red 194
(Cis-form)

2.3.7.4.5 **Perylenes**

Hoechst developed the perylene pigments which are di-imides of perylene-3, 4, 9, 10- tetracarboxylic acid. (Gurdeep, 1990). In the general structure presented below.

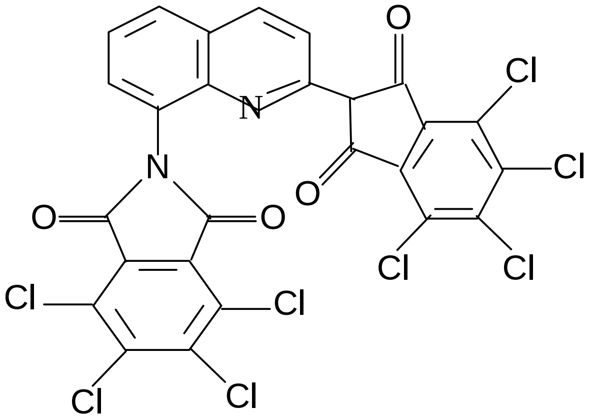
C.I Pigments Red 179 is obtained when R = CH_3



General structure of perylenes

2.3.7.4.6 **Quinophthalones**

Quinophthalone pigments although less extensively commercialized, are required to have a considerably increased molecular size achieved frequently by incorporation of halogen and amide substituents (Gordon, 1983). (Patil, 1974). C. I Pigment Yellow 138 is an example of such a product.



2.3.7.4.7 **Isoindoline pigments**

Although these pigments have been known for sometime, it is only recently that they have been introduced commercially. They are capable of giving yellow through orange to yellowish-red shades. They are related structurally to the tetrachloro isoindolines but, unlike these pigments, the isoindolines give excellent colouristic and fastness properties without requiring the presence of halogen substituents. Examples of these pigments include C. I Pigment Yellow 139 and C. I Pigment Orange 66. They are fast to light and solvent but have low solubility due to intermolecular hydrogen bonding. (Colour Index, 1982).

2.3.7.4.8 **Diketopyrrolopyrroles (DPP)**

The discovery and subsequent commercialization of pigments based on the 1, 4-diketopyrrolo (3, 4 - c) Pyrrole (DPP) system is said to be one of the most important developments in organic pigments of recent years. DPP pigments are capable of providing brilliant saturated red shades of outstanding durability for automotive paint applications. In addition, they have excellent thermal stability, which make them considerably useful in the pigmentation of plastics.

Other important major classes of pigments include Azo methine Pigments, Triarylmethane and related basic dye pigments, metallic Pigments and pearlescent pigments.

2.4 **Properties of pigments**

On the whole, the properties of pigments have been highlighted under individual classes of pigments in this literature and in the preceding introductory chapter. However, for the sake of clarity it is necessary to discuss the requirements of organic pigments in general and azo pigments in particular since the research work is on monoazo yellow pigments, which are synthetic organic pigments.

Gurdeep (1990) enumerated the following requirements (properties) of organic pigments.

(a) **Insolubility in water:** Complete insolubility of pigment in water is rated as excellent. Where pigments have a slight degree of solubility in water or other liquid media they are said to show “bleeding”.

(b) **Insolubility in solvents:** An ideal pigment should be insoluble in all media. However, this condition is not completely fulfilled. Solubility in vehicle or solvent may bring about crystallinity of the pigment causing a change in the colour properties of the paint.

(c) **Fastness to heat:** A pigment should be stable to relatively high temperatures. This applies especially in surface coatings 'cured' or polymerized by heat and in thermosetting colouration. With inferior pigments, chemical decomposition may result from heat treatment, or physical change from one modification to another may occur causing deterioration in hue and other properties.

(d) **Fastness to light:** The most important criterion by which pigments are evaluated is fastness to light, which depends on the medium in which the pigments are dispersed. In general, pigments are less fast to light in pale tints than in dark tints.

(e) **Fastness to acids:** Pigments must be acid-fast if they are to be employed in acid media or if they are to be exposed to acid vapours.

(f) **Fastness to alkalis:** Pigments must be alkali-fast if they are to be used in the manufacture of distempers or the colouration of plaster (masonry) surfaces.

(g) **Ease of dispersion/dispersion stability:** An ideal pigment should be easily dispersible in the application medium.

(h) **Aesthetic appeal:** It is an important property of a pigment that it should have a good appeal to the eyes.

It is pertinent to mention however, that, one particular pigment cannot fulfill all the requirements mentioned above. To satisfy all these requirements various organic pigments have been developed based on most of the different classes of dyestuffs such as lakes of acid or anionic dyes, coumarin dyes, formazin dyes, cationic dyes for synthetic fibres, anthraquinone based dyes, cyanine dyes etc. (Gurdeep, 1990).

In a related development Norbert (1971). stated that the demands made on the light fastness of pigments vary considerably according to the purpose for which they are intended. For coloured articles, which are to be used out-doors, the weathering fastness of a pigment is even more decisive than its light fastness since in addition to light, alternating temperatures and atmospheric humidity affect the performance of pigments.

The fact that some plastics themselves are prone to discolouration under the influence of light must be taken into account when the fastness to light and weathering of a pigment is assessed. The yellowing of inadequately stabilized PVC or polyurethane are examples. The heat stability of pigments is influenced by similar factors.

Another important criterion for determining the suitability of a pigment is its fastness to migration in a given plastic. Migration occurs in different forms and a distinction is made between blooming, bleeding and the “plate-out” effect.

“Chalking”, according to Norbert (1971). can be caused by different factors, and is frequently included among the various manifestations of migration.

Blooming refers to the migration of the pigment out of the plastic. A dusty film forms on the surface of the coloured article within a few days of its manufacture or often only much later. This film can be wiped off but reappears after some time.

This very troublesome phenomenon seems to be caused by a certain solubility of the pigment in the plastic compound (or, in the case of plasticized PVC, in the-plasticizer). Blooming like bleeding occurs only with organic dyes and pigments and not with inorganic pigments. Another contributory factor appears to be the wettability of the pigment by the polymer, since blooming is encountered very frequently with the virtually non-polar polyolefins while polystyrene, polymethylmethacrylate and polyester casting resins can be coloured even with soluble dyes.

The concentration of the pigments in the polymer also influences its tendency to bloom. The lower the concentration of pigment the higher the risk of blooming generally.

The “plate-out effect” (Norbert, 1971). is related to blooming and refers to the migration of pigments to the surface and its deposition on the machine during processing. The pigment concentration, the processing temperature and the presence of lubricants and other auxiliaries also influence this phenomenon. The tendency of pigment “to plate-out” increases with increasing pigment concentration (as opposed to blooming) and rising processing temperature.

Chalking which is similar to blooming, is observed mainly with the α modification of titanium dioxide (anatase) under the influence of weathering.

Bleeding is the migration of a pigment from a pigmented plastic into an adjacent medium. This phenomenon is most often encountered when a pigmented plasticised PVC film comes into contact with a similar unpigmented or differently coloured film and is attributed to a certain degree of solubility of the pigment in the plasticizer. The same characteristic is responsible for the bleeding of pigments from packaging materials into the packed article (foodstuffs, cosmetics, washing – up liquid, etc). (Norbert, 1971).

In general it can be said that all pigments which bloom will also bleed. However, many pigments are known to bleed in plasticized PVC but are fast to blooming and can therefore safely be used for many purposes. It should also be noted that none of the fastness properties mentioned hitherto – heat stability, fastness to light, weathering and migration – is a material constant as are melting point and specific gravity but that all of them vary considerably according to the type of plastic to be pigmented, the pigment concentration, the presence or absence of titanium dioxide, fillers and plasticizers, etc, and finally the processing conditions.

Certain other properties beside the above fastness properties must be taken into account in some specialized fields of application. For instance, it is important that the pigment should be compatible with other additives in the plastic compound and that it should not impair the physical and mechanical properties of the material.

Thus, pigments for colouring cable sheathing compounds must not impair the dielectric properties of PVC compounds. Further examples of the harmful effect that an unsuitable pigment may have on the coloured compound are the accelerated degradation of unplasticized PVC by iron oxide pigments and the reaction between sulphur-containing stabilizers and lead – containing pigments.

Certain types of articles, e.g., children’s toys and film sheeting, bottles, etc, used for packaging foodstuffs, may only be coloured with physiologically harmless pigments; lead - containing pigments such as chrome yellow and molybdate red are not permissible for this application. (Nobert, 1971).

The basic requirements of colourants are: (SDC, 1977). rapid dispersability, fineness or tinting strength, resistance to temperature up to 200^0C in the presence of metallic oxides and sulphur, optionally in contact with steam, and freedom from oxidizing catalytic impurities (copper and manganese salts).

The physical condition of a pigment is a matter of considerable importance since it may affect ease of incorporation into the medium, hue, tinctorial strength, transparency or opacity, the capacity to absorb the vehicle and the rheology of the resulting system. (Feitknecht, 1967). Chemical interaction between pigment and medium may occur in some instances e.g. if a basic pigment such as zinc oxide is used with medium of high acid value.

2.5 Application of pigments

Pigments are ideally water insoluble colorants with no capacity for solublization and reoxidation during application. They therefore cannot be applied to textiles by conventional methods. (Nkeonye, 1993).

The application of pigments to fibre relies on the use of a resin or binder to attach the colorant to the fibre surface.

The pigments and resin can be applied to fabric by padding or printing, and afterwards dry heated (baked or cured) during which the resin polymerizes to bind the pigment particles to the surface of the fabric. (Clarke, 1974).

Pigments are principally employed in the manufacture of paints, printing inks and plastics, although they are used to a certain extent in a much wider range of applications including textiles, ceramics, paper and cosmetics (Herbst *et al,* 1987). In contrast to dyes, pigments are highly insoluble colouring materials, which are incorporated into an application medium by dispersion, and they remain as discrete solid particles held mechanically within the polymeric matrix.

In all applications the pigment should be present in the fully dispersed state (ideally this condition is rarely met). (Achi, 1985).

The particles, whether they be in the fully dispersed or aggregated state, will reflect, scatter and absorb light. The difference between the refractive indices of the pigment and the medium in which it is dispersed will therefore, play a part in determining how much of the light will be reflected. The greater the differences between the refractive indices, the greater the rate of reflection and the more opaque the pigment becomes. In the coloration of plastics, the decision whether to use organic or inorganic pigments is not always easy to make. Organic pigments are generally noted for their high tinctorial strength, brilliance of hue and frequently high transparency, whereas inorganic pigments often have superior hiding power. However, the organic pigment range also includes some products which possess excellent hiding power.

Among the inorganic pigments there are some, which have high tinctiorial strength and examples are cadmium yellow and cadmium red pigments. Highly transparent colorations can, however, be achieved only with organic pigments. Under certain conditions it is expedient to combine organic with inorganic pigments. Thus to produce brilliant, opaque colorations, organic pigments are frequently used together with highly opaque inorganic pigments such as titanium dioxide and also chrome yellow, molybdate red or iron oxide in as far as these are suitable for application in the particular type of plastic.

Besides inorganic pigments, only a few organic pigments with outstanding fastness properties can be considered for outdoor applications where maximum fastness to weathering is essential.

The use of organic pigments in strongly reduced shades for outside application is not advisable.

2.5.1 Colouring techniques

As insoluble substances, pigments are not dissolved but are divided as finely as possible and homogeneously dispersed in the plastic compound.

Most pigments are supplied in agglomerated form, i.e. the primary crystals are intergrown at angles and corners and thus cling together more or less strongly. If a pigment is simply mixed with a plastic compound without the application of shear forces, specky, weak and dull colorations are obtained. It is therefore necessary to break down the agglomerates and divide them as finely as possible in the plastic, i.e. disperse them. (Norbert, 1971).

2.5.2 Injection moulding

Nearly all thermoplastics are processed in the form of granules except PVC. Plastic granules intended for injection moulding are first dry blended with the pigment powder by tumbling (10-15 minute at 30-40 r.p.m.). During tumble blending, the polymer granules become electrically charged, which makes the pigment particles adhere to them. The adhesion of the pigment to the polymer granules can be improved by first mixing the latter with a suitable wetting agent (e.g Haftvermittler K 100). (Harris *et al,* 1984). Dry blended material can subsequently be processed in an injection-moulding machine without further dispersing treatment. In conventional piston injection molding machines uniform coloration by the dry blending method can be achieved only with pigments of very soft grain texture, since the plastic granules are merely melted and then injected direct into the mould. During the entire process virtually no shear forces are brought to bear on the material.

2.5.3 Extrusion moulding

Much better results are obtained when the dry blended materials are processed in an extruder. In this machine strong shear forces act on the materials between the extruder screw and the walls of the barrel. These shear forces are also influenced by the screw speed and the strength of the screw. (Harris *et al,* 1984)

These strong shear forces cause extensive breakdown of the pigment agglomerates and thus ensure good pigment dispersion in the plastic and maximum colour yield. The plastic compound, homogeneously coloured in this way, can be either extruded as a rod, or granulated, and in this form it can be further processed on an injection-moulding machine or directly extruded as the final article (pipe, monofilament, cable sheathing, blown film, sheet or plate). With pigments having a very hard grain texture, it may be necessary to repeat the extrusion process.

The same good dispersion as in an extruder can be achieved in a screw injection-moulding machine, a combination of injection moulding machine and extruder, provided that the pre-plastication zone is not too short.

2.5.4 Calendering

High temperatures and take-off speeds characterize film production on a calendar. The shear forces, which occur during this process, are not sufficient to disperse the pigments. Hence, roller mixers, kneaders or extruder are generally installed ahead of the calendar.

On a two–roll mill strong shear forces are created by the two-heated metal friction rollers rotating in contact with each other at different speeds, ensuring that even pigments with a hard grain texture are satisfactorily dispersed, provided that the temperature is not too high. The rough sheet from the roller mixer is then rolled out into film or sheeting on the calender.

Similar conditions exist in the kneader, which is also used for premixing and dispersing. The mixing operation is performed by specially shaped blades, which rotate against one another in a heatable metal casing, thus creating counter flow and the necessary shear forces. (Norbert, 1971).

2.5.5 Processing thermosetting resins

Conditions different from those required for thermoplastics are needed in the processing of thermosetting resins (e.g. phenolic resins, aminoplasts).

Thermosetting resins are sold in powder form and, as they are still incompletely cross-linked at this stage, can be given any required shape. During processing they are forced into moulds under the influence of heat and pressure and are cured. To colour the resin powder, it is mixed or ground in a ball mill together with the pigment and fillers before processing. Particularly fine pigment divisions cannot be achieved by this process and in the compression moulding In the process itself, shear forces are totally absent.

Thermosetting resins can also be processed by a modified injection moulding technique. This method differs from conventional injection moulding in that the material is plasticated at fairly low temperatures in the injection moulding machine and is then forced into a hot mould where curing takes place. (Harris *et al,* 1984).

2.6 Uses Of Pigments

As earlier stated, pigments are used mainly in the coloration of paints, printing inks and plastics. However, they are used to a certain extent in a much wider range of applications including textiles, ceramics, paper, cosmetics and food.

CHAPTER THREE

EXPERIMENTAL WORK

3.1 Equipment

Micro weighing balance

Melting point apparatus (Gallenkamp melting point apparatus)

Magnetic stirrer

Hot plate

Oven

Buchner funnel

Suction pump

One-litre beakers

Stirring rods

Thermometer 0- 360 ^{0}C range

Thermometer 0- 100 ^{0}C range

Watch glasses

Capillary tubes

Buchner flask

Starch – iodide paper

Whatmann filter paper 12.5cm

p^H indicator paper 1 – 14

Pressure pump

250ml beakers

3.2 Chemicals / Reagents

2,4 – Dinitroaniline

o – Niroaniline

m – Toluidine

4– Niroaniline

Acetoacetanilide

Acetoacet – 2,5 – dichloroaniline (2,5 – dichloroacetoacetanilide)

Sodium nitrite

Sodium hydroxide

Sodium acetate

Aniline

Hydrochloric acid

2- ethoxyethanol

Glacial acetic acid

Methanol

β – Naphthol

Conc. sulphuric acid

Urea

Acetone

Ethanol

Benzene

Toluene

Xylene

3.3 Synthesis of pigments

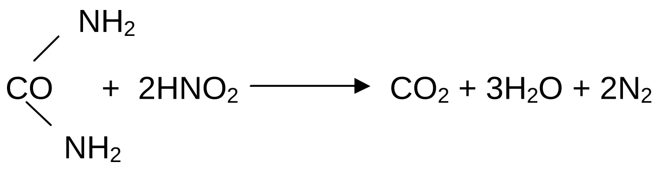
A total of twelve pigments were synthesized in this work. Four pigments were synthesized based on β-naphthol, five based on acetoacetanilide and three based on acetoacet-2,5-dichloroaniline.

The procedures adopted for all the experiments with the exception of diazotization and coupling of 2,4 –dinitroaniline were those of diazotisation and coupling of o-nitro-p-toluidine.

3.3.1 Diazotization of 2,4-dinitroaniline (5g) using conc. H_2SO_4

2.2ml conc. sulphuric acid was placed in a 250ml beaker, cooled to 0°C and 1.9g {0.027moles} of sodium nitrite was slowly added. The mixture was warmed to 70°C while it was stirred to dissolve the nitrite {brown fumes evolved}.

The mixture was cooled to 20°C and then 5g (0.027 moles) of 2,4–dinitroaniline was added slowly with stirring until the reaction for the nitrite was faint. Starch potassium iodide paper was used to detect the presence of nitrous acid using a diluted sample of the reaction charge. Excess nitrite was destroyed by the addition of urea as indicated by the equation below:



$$CO(NH_2)_2 + 2HNO_2 \longrightarrow CO_2 + 3H_2O + 2N_2$$

The diazonium solution was filtered and the filtrate was used immediately.

3.3.2 Diazotization of o-nitroaniline (1g)

In a 250ml beaker, 1g of o-nitroaniline was stirred in 10ml of distilled water at 0^0C to which had been added 2ml (0.6moles) concentrated hydrochloric acid. 0.46g (0.0067moles) of sodium nitrite dissolved in 3.3ml distilled water was added into the reaction charge over 60 minutes with constant stirring.

The beaker was cooled continuously during the course of the reaction in an ice-salt bath at $0\text{-}5^0$C. The solution was filtered off and used immediately.

3.3.3 Diazotization of 4-nitroaniline

Experiment 3.3.2 was repeated using 4-nitroaniline in place of o-nitroaniline.

3.3.4 Diazotization of m-toluidine

Experiment 3.3.2 was repeated using m-toluidine in place of o-nitroaniline.

3.3.5 Diazotization of aniline

Experiment 3.3.2 was repeated using aniline in place of o-nitroaniline.

3.3.6 Coupling of diazotised 2,4-dinitroaniline with β-naphthol

3.2g (0.08 moles) of sodium hydroxide was stirred until dissolved in 128ml of ethanol. 5g representing (0.032 moles) of β-naphthol was added and stirred until fully dissolved. The temperature was lowered to 5 – 8^0C and 2ml glacial acetic acid was added.

The 2,4-dinitroaniline (filtrate) salt was then added from a dropping funnel over a period of 30 min. to the ice-cold coupling component. The mixture was stirred for 1hr to achieve complete coupling. The pigment was filtered, washed with hot water to neutrality and dried at 60^0C. The yield, colour and melting points were recorded in table 1.

3.3.7 Coupling of diazotized 2,4-dinitroaniline with acetoacetanilide

Experiment 3.3.6 was repeated with acetoacetanilide in place of β-naphthol.

3.3.8 Coupling of diazotised 2,4 dinitroaniline with acetoacet-2,5-dichloroaniline

Experiment 3.3.6 was repeated with acetoacet-2,5 dichloroaniline in place of β-naphthol.

3.3.9 Coupling of diazotized o-nitroaniline with β-naphthol

In a 250 ml beaker 1g β-naphthol was dissolved by stirring in 17ml of distilled water to which 0.3g (0.0075 moles) of sodium hydroxide had been added.

Dilute (0.1m) HCl was added until the solution was just titan to yellow (below p^H 12). 1.47g (0.0179 moles) sodium acetate was added and the temperature was adjusted to 10 ± 2^0C.

The o-nitroaniline diazonium salt was added over 60 minutes with constant stirring into the reaction mixture. The end point of coupling was tested with filter paper by spotting the reaction charge on to it until a ring was formed.

3.3.10 **Coupling of diazotised o-nitroaniline with acetoacetanilide**

Experiment 3.3.9 was repeated with acetoacetanilide in place of β-naphthol.

3.3.11 **Coupling of diazotised o-nitroaniline with acetoacet-2,5-dichloroaniline**

Experiment 3.3.9 was repeated with acetoacet-2,5 dichloroaniline in place of β-naphthol.

3.3.12 **Coupling of diazotized 4-nitroaniline with β-naphthol**

Experiment 3.3.9 was repeated with 4-nitroaniline in place of o-nitroaniline

3.3.13 **Coupling of diazotised 4-nitroaniline with acetoacetanilide**

Experiment 3.3.12 was repeated with acetoacetnilide in place of β-naphthol

3.3.14 Coupling of diazotised 4-nitroaniline with acetoacet-2,5-dichloroaniline

Experiment 3.3.12 was repeated with aceotacet-2,5-dichloroaniline in place of β-naphthol.

3.3.15 Coupling of diazotised m-toluidine with β-naphthol

Experiment 3.3.9 was repeated with m-toluidine in place of o-nitroaniline

3.3.16 Coupling of diazotised m-toluidine with acetoacetanilide

Experiment 3.3.15 was repeated with acetoacetanide in place of β–naphthol

3.3.17 Coupling of diazotised aniline with acetoacetanilide

Experiment 3.3.9 was repeated with aniline in place of o-nitroaniline and acetoacetanilide in place of β-naphthol

3.4 Recrystallization of the synthesized pigments

Pigments A, D, G and J were purified in each case by dissolving in 20 mls of glacial acetic acid to remove insoluble materials and other impurities, the precipitate pigment was filtered, washed thoroughly with hot water and finally dried in an overn at 60^0C.

Pigments B, C, E, F, H, I and K were recrystallized from glacial acetic acid and 2-ethoxy ethanol respectively.

3.5 Determination of melting point

The melting points of the synthesized pigments were determined using the Gallenkamp melting point apparatus.

The values obtained are shown in Table 4.1

3.6 Visible absorption measurements

The peak of maximum absorption wavelength (λ_{max}) for each pigment was determined in acetone using a spectrophotometer (Unicam SP 800). Using the λ_{max} obtained, the absorption was recorded for a known concentration of each pigment. The results are shown in Table 4.2.

3.8 Determination of molar extinction coefficient

The molar extinction coefficient (ε), which is a constant for each molecule at any given wavelength, represents the absorbance of 1cm thickness of a medium containing 1 mole of the absorbing substance per litre (Giles, 1974).

(ε) was calculated using the relationship

$\mathrm{Log}_{10}(I_0/I) = \varepsilon cl$

Where $\log_{10}(I_0/I)$ = absorbance (A) or optical density

:. $A = \varepsilon cl$

$$\varepsilon = \frac{A}{cl}$$

where ε = molar extinction coefficient

A = absorbance or optical density

c = pigment concentration in moles /litre

l = path length of the cell (1cm)

Molar extinction coefficient was calculated based on the concentration of the pigments that went into solution, for those pigments that were partially soluble in acetone.

The calculated molar extinction coefficients were recorded in Table 4.2

3.9 Assessment of synthesized pigments:

3.9.1 Solubility test

3.9.1.1 Solubility in water

The pigments were tested for solubility in water by shaking 0.01g of each pigment in 20mls of water. The results are shown in Table 4.3.

3.9.1.2 Solubility in solvents

The pigments were tested for solubility in selected solvents namely benzene, toluene, xylene, methanol, acetone, 2-ethoxyethanol by shaking 0.01g of each pigment in 10mls of each solvent. The results are also shown in Table 4.3.

3.9.1.3 Solvent test

The pigments were tested for resistance to bleeding as follows:

A pigment suspension was prepared by vigorously shaking for 1minute 0.5g of the pigment in a test tube with 10ml each of acetone, white spirit, ethanol and 2-ethoxyethanol at room temperature.

A second suspension was prepared as above, then boiled (with precaution) for 1minute. 1 to 3 drops of the dispersion was spotted on a filter paper and the colour of the resulting patch was observed (Nkeonye, 1990). The test samples were treated in the same way and results are shown in Table 4.4

3.10 Application of pigments to substrates

The synthesized pigments were applied onto five substrates, viz:

100% cotton (cellulosic)

100% polyester (plastic)

100% wool (protein)

35/65% cotton/polyester (blend)

White paper (density 80g/m^2) (cellulosic)

The pigments were applied by the following methods

(a) Padding

(b) Resin Bonding

In the first method, printing of cellulose was achieved by the following stages:

a) Impregnation of the cloth with an alkaline solution of Naphthol AS and drying.

b) Printing with a thickened paste of the pigment

c) Washing off i.e. hot alkaline soap treatment

Recipe for Padding with Naphthol

1g	Naphthol AS was pasted with
2ml	methylated spirit followed by
2ml	boiling water until completely wet out then add
1ml	Caustic soda 18% then bulked with hot water to
100ml	

Stage I: Procedure for padding with naphthol

The fabric was padded in the solution (prepared above) for 30minutes at room temperature, then squeezed using pad mangle. The fabric was cut into two equal halves. One half was ironed immediately and the other half was steamed for 15minutes before printing

Stage II Printing with a thickened paste of the pigment

The pigment printing paste was made up of the following:

2 parts	Pigment was pasted with
10 parts	water below 30^0C followed by
50 parts	thickening agent (locust bean)
2 parts	acetic acid was added and the paste was bulked to
100 parts	

Printing: The print paste was applied to the previously padded fabric using flat screen-printing method.

Fixation: Was achieved by baking at 150^0C for 5 minutes.

Stage III Washing off after treatment.

After printing, the fabric was washed with 2g/l soap to remove unfixed pigment and to improve the hue of the pigment; then thoroughly washed with warm water and dried.

(b) Recipe for the Resin-binding method (stock emulsion thickening)

Emulsifier	200 parts
Thickening (sodium alginate)	50 parts
Water	150 parts
Imperon binder	200 parts
White spirit	300 parts
Sodium carbonate	20 parts
Urea	10 parts
Resist salt L	20 parts
Bulked to	1000 parts

The print paste was made up of:

2 parts	Pigment pasted with
10 parts	water below 30^0C followed by
50 parts	Stock thickening and
2 parts	acetic acid (40%) and then bulked to
100 parts	

In the resin binding method printing was carried out by applying the printing paste onto the substrate (fabric) using flat screen. This was immediately followed by drying in an open atmosphere before baking at 140^0C for10 minutes using the Werner Mathis AG curing machine. The fabric was finally given an after treatment by washing in 2g/l solution of caustic soda to get rid of unfixed pigment molecules as well as to improve the hue of the printed sample.

3.11 Wash fastness test

The printed samples were subjected to IS0 3 wash fastness test by the following procedures:

The specimens were prepared by cutting the printed samples into 10cm X 4cm dimensions. These samples were made into composites by stitching a test specimen made up of the printed sample placed in between white cotton and wool of dimensions 5cm X 4cm. The composite was agitated in solution made up of the following:

5g/l soap solution

2g/l sodium carbonate

Liquor ratio 50:1

The washing was carried out in the linitest machine at 60 ± 2°C for 30 minutes. The composite was then separated and dried. (SDC, 1965)

3.11.1 Assessment of change in colour

Grey scale for evaluating change in colour was used to determine the change in colour after the washing test. The procedure involved comparing the degree of contrast between the originally printed sample and the specimen tested, compared to the degree of contrast between the pairs of colours in the standard grey scale for assessing change in colour. The fastness rating of the specimen under test is the number of this grey scale contrast.

The result of change in colour are in Tables 4.5, 4.6, 4.9, 4.10, 4.13, 4.14, 4.17, 4.18, 4.21, 4.22, 4.25 and 4.26.

3.11.2 Assessment of staining

The white cotton and the stained specimen were assessed using the same procedure for assessing change in colour. The result are shown in Tables 4.4. 4.5, 4.6, 4.9, 4.10, 4.13, 4.14, 4.17, 4.18, 4.21, 4.22, 4.25 and 4.26.

3.12 Light Fastness Test

Light fastness test of the printed samples was carried by the use of the Xenon arc light fastness instrument.

The procedure involved aligning both the eight dyed wool standards together with the printed specimens on a card, which was later attached to a stainless steel metal strip and then inserted into a compartment, which was maintained at a constant relative humidity by the use of distilled water during exposure. The compartment was then placed into position along the radial exposure chamber. Exposure was carried out for 48hours until the last specimen to fade had faded to the extent of standard three of the standard grey scale for evaluating change in colour. The test was then terminated. (SDC, 1965).

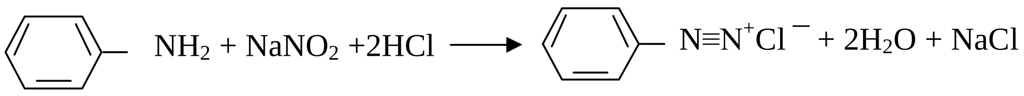
The rating of the printed sample is that of the wool dyed sample, which faded to the same extent as the specimen at the same time. The result of the light fastness rating are shown in Tables 4.7, 4.8, 4.11, 4.12, 4.15, 4.16, 4.19, 4.20, 4.23, 4.24, 4.27 and 4.28.

CHAPTER FOUR
RESULTS AND DISCUSSIONS

4.1 Introduction

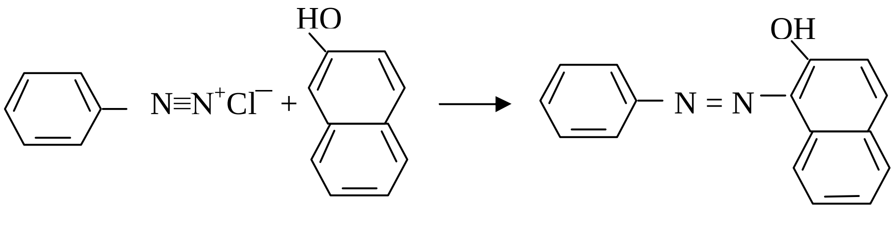
Classically, azo comounds are formed by diazotising a primary aromatic amine, and then coupling this to a coupling component, typically a derivative of β-naphthol, pyrazolone or acetoacetanilide.

The diazonium salt is formed in an acid medium; e.g.



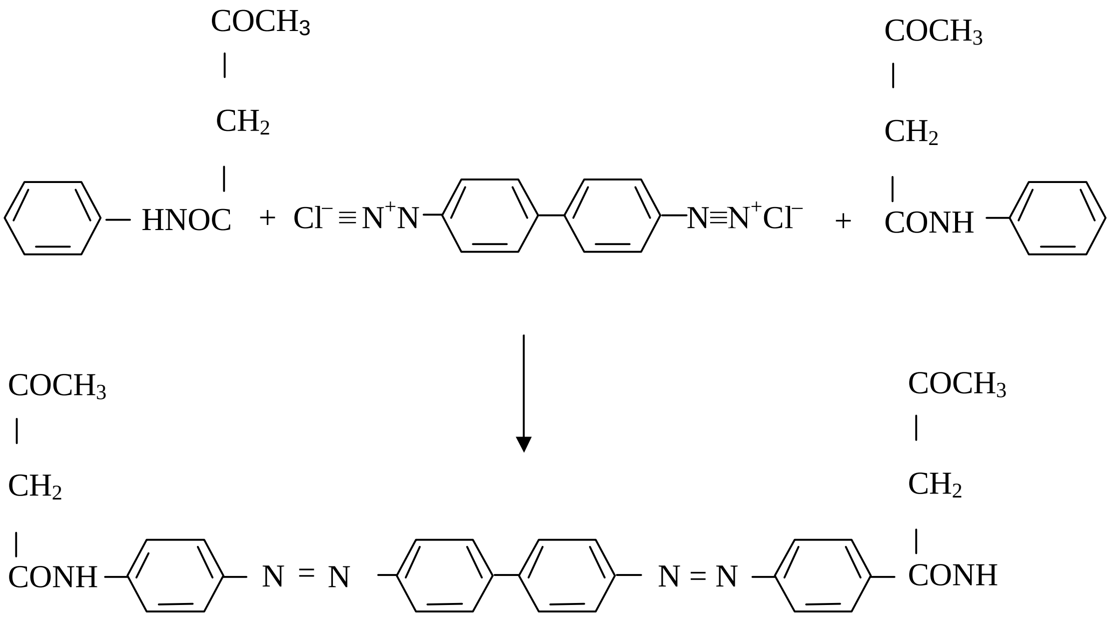
Diazonium salt

The diazonium salt is then coupled to β- naphthol to produce an azo colour.



Azo colour

The disazo pigments are formed in the same manner as monoazo pigments but require two molecules of the coupling component for complete coupling, e.g., the coupling of 2 molecules of acetoacetanilide with tetrazotised benzidine:



4.2 Synthesis of pigments

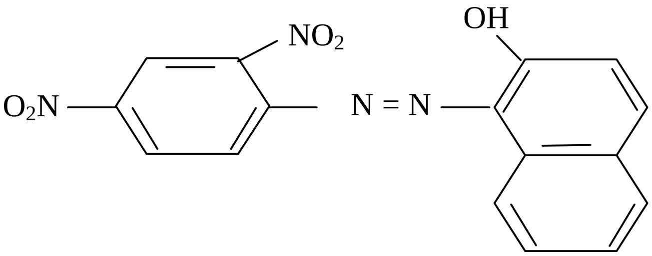
All the twelve pigments were synthesized based on general principle of diazotisation and coupling as shown in the experimental work.

The yield, color and melting points of the pigments are shown in Table 4.1.

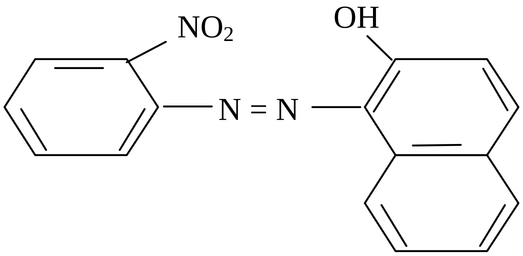
Table 4.1. Yield, colour, melting point, and molecular weight of pigments

Pigment	Diazo–component	Coupling component	Quantity (g)	Yield (%)	Colour	Melting point(^{0}c)	Mol.wt (g)
A	2,4 - Dinitro aniline	β – naphthol	5	85.7	Orange	301	338
B	2,4 – dinitro aniline	Acetoacetanilide	5	79.3	Yellow	291	371
C	2,4 – dinitro aniline	Acetoaceta-2,5-dichloroaniline	1	72.7	Greenish - yellow	299	440
D	o-nitroaniline	β-naphthol	1	65.2	Orange	192	293
E	o-nitroaniline	Acetoacetanilide	5	74.2	Bright - yellow	190	326
F	o-nitroaniline	Acetoaceta-2,5-dichloroaniline	5	74.0	Greenish - yellow	191	395
G	4-nitroaniline	β--naphthol	1	50.8	Orange	254	293
H	4-nitroaniline	Acetoacetanilide	1	57.7	Greenish-yellow	252	326
I	4-nitroaniline	Acetoace-2,5-dichloroaniline	1	60.5	Greenish-yellow	256	395
J	m-toluidine	β-naphthol	5	52.8	Purple	253	262
K	m-toluidine	Acetoacetanilide	5	57.7	Yellow	250	295
M	Aniline	Acetoacetanilide	1	64.5	Orange	252	281

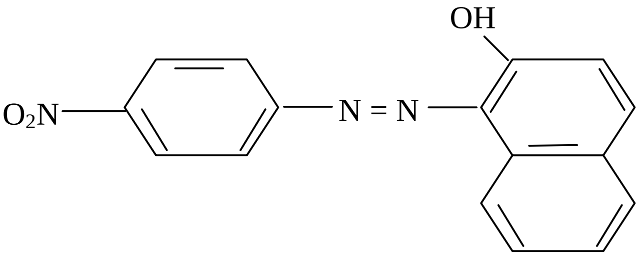
The yield obtained was good and the melting points corresponded with what was reported in the literature, relatively low. Pigments A, D, G, and J were derived from β-naphthol and their structures are shown as below:



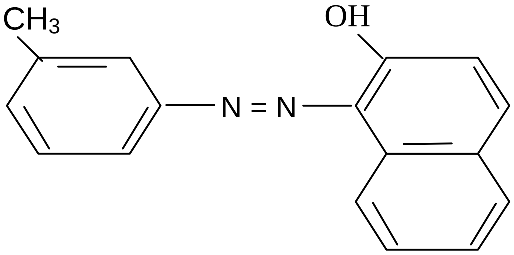
PIGMENT A



PIGMENT D

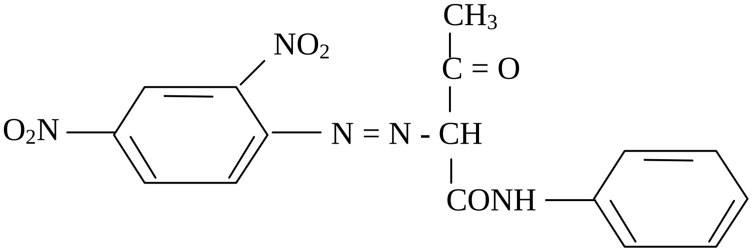


PIGMENT G

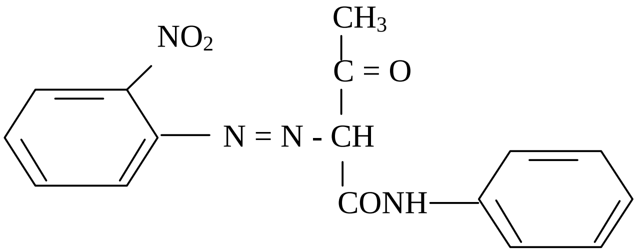


PIGMENT J

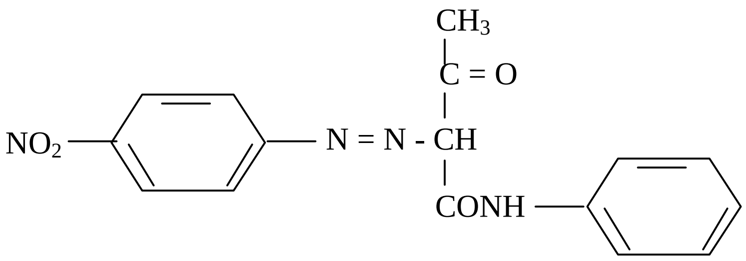
Pigments B, E, H, K and M were synthesized from acetoacetanilide and their structures are as follows:



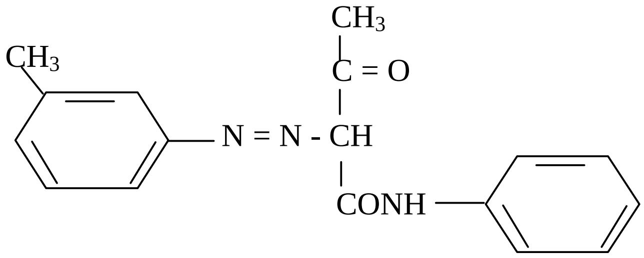
PIGMENT B



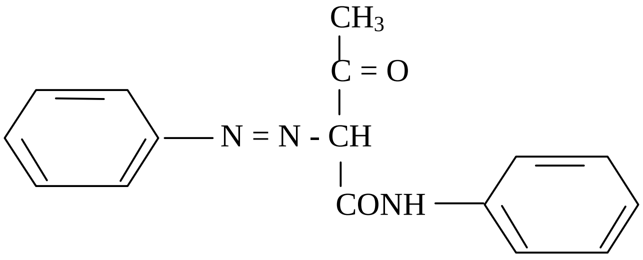
PIGMENT E



PIGMENT H

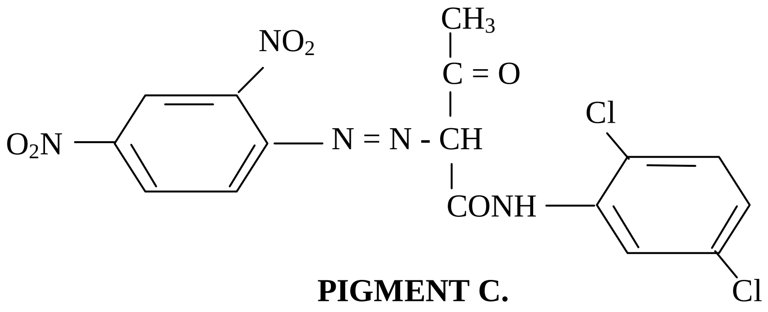


PIGMENT K

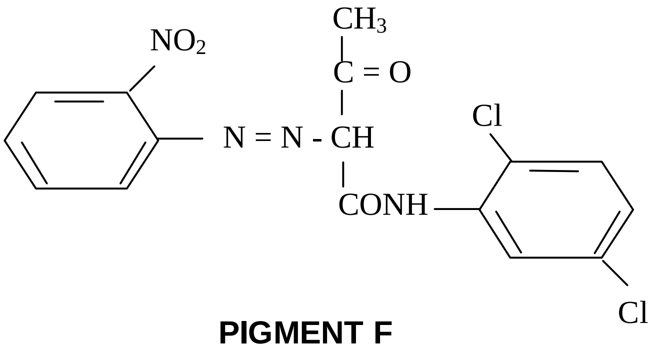


PIGMENT M

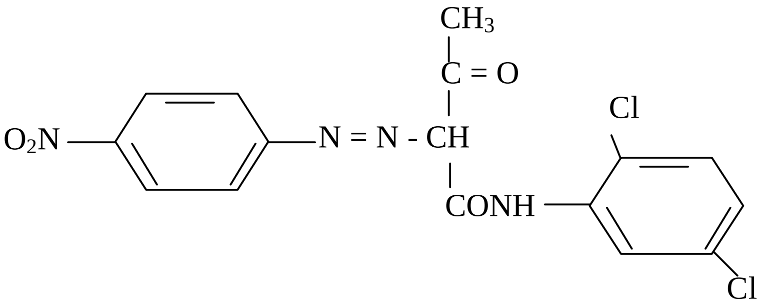
Pigments C, F and I were synthesized based on acetoacet –2,5 – dichloroaniline, and their structures are as follows:



PIGMENT C.



PIGMENT F



PIGMENT I.

The yields obtained from pigments A - M as summarized in Table 1 were good though not very high and this could be attributed to the rupturing of the benzene ring by the electron strength of the NO_2 groups, in the cases of the nitro compounds.

The diazotisation of 2, 4 – dinitroaniline was carried out with normal sulphuric acid instead of sulphamic acid which is considered to be more suitable for diazotisation of 2, 4-dinitroaniline.

The expected orange pigment crystals resulting from the diazotisation of the arylamines, 2, 4–dinitroanaline, o-nitroaniline, 4-nitroaniline and coupling with β-naphthol then consequent recrystallisation from glacial acetic acid was a positive result as indicated by the synthesized pigments A, D and G.

The bright-yellow and greenish-yellow monoazo pigments obtained from acetoacetanilide and acetoacet – 2, 5 – dichloroaniline respectively, are quite in consonance with literature (Christie, 1993), (Achi, 1985), (Bello, 1996).

4.3 Recrystallisation of the Synthesized Pigments

Most of the synthesized pigments with the exception of pigment A did not recrystallize fully in glacial acetic acid and none at all recrystallized from benzene or toluene. Only pigments B, C, E, F, H and I partially recrystallized in 2–ethoxyethanol.

The incomplete recrystallization in the above solvents might mean the synthetised pigments had some impurities before their melting points were determined. This might explain the reason why the melting points of some of the pigments did not fall within the exact range as provided in literature. (Achi, 1985), (Bello, 1996).

4.4 Visible absorption spectroscopic measurements

Visible absorption spectra of the pigments were measured in acetone. The molar extinction coefficient was calculated and the results are as shown in Table 4.2

Table 4.2 Visible absorption spectra of pigments

Pigment	Concentration in moles/litre x 10^{-4}	Absorbance at λ_{max}	λ_{max} (nm)	Molar extinction coefficient l mol^{-} cm^{-1} x 10^{4}
A	0.075	0.266	449.3	3.547
B	0.125	0.245	446.1	1.960
C	0.050	0.222	429.7	4.440
D	0.180	0.270	482.4	1.500
E	0.075	0.255	465.3	3.400
F	0.125	0.237	432.5	1.896
G	0.075	0.271	488.3	3.611
H	0.150	0.266	478.5	1.780
I	0.075	0.239	435.0	3.187
J	0.100	0.299	498.5	2.990
K	0.180	0.248	456.4	1.378
M	0.180	0.240	439.6	1.333

Pigment A absorbed at 479nm with orange colour. Pigment D absorbed at 482nm indicating a bathochromic shift of 2.7nm. Pigment G absorbed at 488nn showing a bathochromic shift of 6nm.

The corresponding bathochromic shifts were due to reduction in the number and alteration of positions of the electron withdrawing (NO_2) group from ortho in o-nitroaniline to para position in 4-nitroaniline. Pigment J absorbed at a much higher wavelength (498.5nm) giving a purple colour when compared to pigments A, D, G. This could be attributed to the increase in conjugation of the pigment molecule as a result of incorporation of a methyl (CH_3) group to the aniline structure. Pigments B, E and H were synthesized by using the same arylamines 2,4 dinitroaniline, o-nitroaniline and 4 nitroaniline respectively and coupling with acetoacetanilide instead of β-naphthol in the cases of pigments A, D and G.

Pigments B, E and H absorbed at 446.1nm, 465.3nm, and 478.5nm respectively. These values also show bathochromic shifts of 19.2nm and 13.5nm respectively. However, the absorption spectra of the pigments synthesized from acetoacetanilide as coupling agent are generally lower than those synthesized from β-napthol as coupling agents. This is due to the fact that acetoacetanilide has weak influence on the arylamine benzene ring such that it could not create high resonance compared to β-napthol. In effect, lower resonance means decrease in absorbance (i.e. shorter wavelength). (Gudeep, 1990).

When acetoacet-2,5-dichloroaniline was used to couple 2,4-dinitroaniline it gave pigment C which absorbed at 429.7nm and it appeared greenish-yellow in colour. Pigment F was obtained by replacing 2,4-dinitroaniline with o-nitroaniline while maintaining the same coupling component acetoacet-2,5-dichloroaniline. It absorbed at 432.5nm giving a slight bathochromic shift of 2.8nm. Its colour was also greenish-yellow. Pigment I was obtained by replacing o-nitroaniline with 4-nitroaniline and it absorbed at 435.0nm indicating a bathochromic shift of 5.7nm. It also appeared greenish yellow in colour.

The reasons for the bathochromic effects of pigment C, F and I are the same for pigments A, D and G; that is, reduction in the number of electron withdrawing (NO_2) groups as well as altering their positions.

The presence of two halogen, chlorine (Cl) atoms in acetoacet-2,5-dichloroaniline was responsible for the greenish-yellow colour of pigments C, F and I. The λ_{max} (Table 4.2) of these pigments were however, expected to be greater than those of their counterparts B, E, H and K. They gave more intense colour. But this distinction was not obtained. This is however, difficult to explain. From the on-going analysis it could be deduced that pigments produced using β-naphthol as coupling components appeared deeper in shade and gave greater bathochromic effects than those produced using acetoacetanilide and acetoacet-2,5-dichloroaniline as coupling components for reasons earlier explained.

Also the presence of two chlorine atoms (halogen groups) on acetoacet-2,5-dichloroaniline improved the shade of pigments obtained from it when compared to acetoacetanilide without halogen substituent(s).

The molar extinction coefficient, which is a measure of the amount of light being absorbed by a compound in solution, was calculated for each pigment. From the results in Table 4.2 it could be observed that pigments possessing higher molar extinction coefficient with deeper shades appeared brighter on the fabric. This is explained by the fact that they transmit more light and have narrow absorption bands with sharp peaks when compared with the other pigments.

4.5 Solubility test

None of the synthesized pigments dissolved in water (cold or warm), Pigments A, D, G and J were insoluble in benzene, toluene, xylene and methanol. They were partially soluble in acetone and 2-ethoxyethanol.

Pigments B, C, E, F, H, I K and M were insoluble in benzene, toluene, xylene methanol, partially soluble in 2-ethoxyethanol and completely soluble in acetone. The results of the solubility test are shown in Table 4.3.

Table 4.3 Solubility of pigments in selected solvents

PIGMENT	SOLVENT						
	WATER	BENZENE	TOLVENE	XYLENE	METHANOL	ACETONE	2-ETHOXYETHANOL
A	I	I	I	I	I	PS	PS
B	I	I	I	I	I	S	PS
C	I	I	I	I	I	S	PS
D	I	I	I	I	I	PS	PS
E	I	I	I	I	I	S	PS
F	I	I	I	I	I	S	PS
G	I	I	I	I	I	PS	PS
H	I	I	I	I	I	S	PS
I	I	I	I	I	I	S	PS
J	I	I	I	I	I	PS	PS
K	I	I	I	I	I	S	PS
M	I	I	I	I	I	S	PS

KEY TO TABLE 3

I	Insoluble
PS	Partially soluble
S	Soluble

Table 4.4 comparison of solvent test on filter paper and test samples

Pigment	Solvent	COLOUR OF RESULTING PATCH					
		Filter Pigment	Cotton	Polyester	Wool	Cotton/Polyester	Paper
A	Acetone	O	O	O	O	O	O
	White spirit	PO	NSC	NC	NC	NC	PO
	2-ethoxyethanol	PO	PO	PO	PO	PO	PO
B	Acetone	Y	Y	Y	Y	Y	Y
	White spirit	PY	NSC	NSC	NSC	NSC	PY
	2-ethoxyethanol	PY	PY	PY	PY	PY	PY
C	Acetone	GY	GY	GY	GY	GY	GY
	White spirit	PY	NSC	NSC	NSC	NSC	PY
	2-ethoxyethanol	PY	PY	NSC	NSC	PY	PY
D	Acetone	O	O	O	O	O	O
	White spirit	PO	PO	PO	PO	PO	PO
	2-ethoxyethanol	PO	PO	PO	PO	PO	PO
E	Acetone	Y	Y	Y	Y	Y	Y
	White spirit	Y	PY	PY	PY	PY	Y
	2-ethoxyethanol	Y	Y	Y	Y	Y	Y
F	Acetone	GY	LG	LG	LG	LG	GY
	White spirit	Y	PY	PY	PY	PY	Y
	2-ethoxyethanol	GY	GY	GY	GY	GY	GY
G	Acetone	O	O	O	O	O	O
	White spirit	PO	NSC	NSC	NSC	NSC	PO
	2-ethoxyethanol	PO	PO	PO	PO	PO	PO
H	Acetone	GY	Y	Y	Y	Y	GY
	White spirit	Y	Y	NSC	NSC	NSC	Y
	2-ethoxyethanol	PY	PY	PY	PY	PY	PY
I	Acetone	GY	GY	GY	GY	GY	GY
	White spirit	PY	PY	PY	PY	PY	PY
	2-ethoxyethanol	Y	PY	PY	PY	PY	Y
J	Acetone	P	P	P	P	P	P
	White spirit	NSC	NSC	NSC	NSC	NSC	NSC
	2-ethoxyethanol	NSC	NSC	NSC	NSC	NSC	NSC
K	Acetone	Y	Y	Y	Y	Y	Y
	White spirit	PY	NSC	NSC	NSC	NSC	PY
	2-ethoxyethanol	PY	PY	PY	PY	PY	PY
M	Acetone	Y	Y	Y	Y	Y	Y
	White spirit	PY	PY	PY	PY	PY	PY
	2-ethoxyethanol	Y	Y	Y	Y	Y	Y

Key to table 4.4

Y	Yellow
GY	Greenish yellow
PY	Pale yellow
O	Orange
PO	Pale orange
P	Pink
NC	No change in colour
NSC	No significant change in colour

4.6 Wash fastness properties

All the printed fabrics namely cotton, polyester, wool and cotton/polyester blend were assessed for wash fastness test using ISO 3 standard procedure.(SDC, 1978). The printed fabrics were assessed for both change in shade and staining of the adjacent fabrics and the results are as shown in Tables 4.5, 4.6, 4.9, 4.10, 4.13, 4.14, 4.17, 4.18, 4.21, 4.22, 4.25 and 4.26.

Table 4.5. Wash fastness of padded and steamed samples of pigments derived from β-Naphthol

ENT	SUBSTRATE							
	COTTON		POLYESTER		WOOL		COTTON/POLYESTER	
	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE
A	4	4 – 5	4	3 - 4	3	3	3	3 - 4
D	4	3 - 5	4	4	3 - 4	3 - 4	4	4
G	3	3	4	4	3	3 - 4	3	3 - 4
J	3	3	3 - 4	4	2 - 3	3	3	3 - 4

Table 4.6. Wash fastness of padded and baked samples of pigments derived from β-Naphthol

PIGMENT	SUBSTRATE							
	COTTON		POLYESTER		WOOL		COTTON/POLYESTER	
	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE
A	3 – 4	3 – 4	4	3 - 4	4 – 5	4	3 – 4	4
D	4	4	3 – 4	3	4 - 5	4 - 5	3 – 4	3 - 4
G	2 – 3	3	3	3	4	4	3	3
J	2 – 3	2 - 3	3	2 - 3	3	3	3	2 - 3

Table 4.7 Light fastness ratings of padded and steamed samples for pigments derived from β-Naphthol

PIGMENT	SUBSTRATE				
	COTTON	POLYESTER	WOOL	COTTON/POLYESTER	PAPER
A	4	4 - 5	4 – 5	5	4 – 5
D	4	4 – 5	4 – 5	5	5
G	4 - 5	5 - 6	5	4 – 5	5
J	3 - 4	4	4	3	4

Table 4.8 Light fastness ratings of padded and baked samples for pigments derived from β-naphthol

PIGMENT	SUBSTRATE			
	COTTON	POLYESTER	WOOL	COTTON/POLYESTER
A	4 - 5	4 - 5	6	5
D	4	5 - 6	6	5
G	4	4 - 5	5 - 6	4 - 5
J	3 - 4	4	5	4

Table 4.9 Wash fastness of resin-bonded and steamed samples for pigments derived from β- Naphthol

ENT	SUBSTRATE							
	COTTON		POLYESTER		WOOL		COTTON	COTTON/POLYESTER
	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE
A	4	4	4	3-4	3	2-3	3	3
D	3	3-4	4	3	3	3	4	3-4
G	3	2-3	3-4	3-4	3	3	3	3
J	2-3	3	3-4	3	2-3	3	3	2-3

TABLE 4.10 Wash fastness of resin-bonded and baked samples for pigments derived from β- Naphthol

PIGMENT	SUBSTRATE							
	COTTON		POLYESTER		WOOL		COTTON	PLYESTER
	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE
A	2	3	2	3-4	4	3	3	3-4
D	3	2-3	3	2-3	4	4	3-4	3
G	2	3	2-3	3	3-4	3-4	3	3
J	2	2-3	2	2-3	3	2-3	2	2-3

Table 4.11 Light fastness ratings of resin-bonded and steamed samples for pigments derived from β-naphthol

PIGMENT	SUBSTRATE				
	COTTON	POLYESTER	WOOL	COTTON/POLYESTER	PAPER
A	4-5	3	5	4-5	4
D	3	4	5	5	5
G	3-4	4	3-4	3-4	4
J	2-3	3	3-4	3	4

TABLE 4.12 Light fastness ratings of resin-bonded and baked samples for pigments derived from β-Naphthol

PIGMENT	SUBSTRATE				
	COTTON	POLYESTER	WOOL	COTTON/POLYESTER	PAPER
A	5	4	5	4 – 5	4
D	3 – 4	4	5 – 6	5	5
G	3 – 4	4	3 – 4	4	4 – 5
J	3	3	3 – 4	3	4

Table 4.13 Wash fastness of padded and steamed samples of pigments derived from Acetoacetanilide

PIGMENT	SUBSTRATE							
	COTTON		POLYESTER		WOOL		COTTON/POLYESTER	
	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE
B	3 – 4	3	2 – 3	2	3 – 4	3	4	3 – 4
E	3 – 4	3	3	3	4	3	4	3
H	3 – 4	3	4	3 – 4	4	3 – 4	4	3
K	3	2 - 3	3 – 4	3	3 – 4	3	3	3
M	2 – 3	2	3	2 – 3	3	2 – 3	3	2 - 3

TABLE 4.14 Wash fastness of padded and baked samples of pigments derived from Acetoacetanilide

PIGMENT	SUBSTRATE							
	COTTON		POLYESTER		WOOL		COTTON/POLYESTER	
	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE
B	3	3	2 – 3	2	3	3	3	3
E	3	3	3	2 – 3	3 – 4	3	3 – 4	3
H	3	2 – 3	4	3 – 4	3 – 4	3 – 4	4	3
K	3	2 - 3	3	3	3	3	3	2 – 3
M	3	2	2 – 3	2 – 3	3	2 - 3	3	2 - 3

Table 4.15 Light Fastness ratings of padded and steamed samples for pigments derived from Acetoacetanilide

PIGMENTS	SUBSTRATE				
	COTTON	POLYESTER	WOOL	COTTON/POLYESTER	PAPER
B	4 – 5	4	4	4	5
E	4	4 – 5	5	5 – 6	5 – 6
H	4 – 5	4	4 – 5	4	4
K	4	4 – 5	4	4	3 – 4
M	2 – 3	3	3	3	3 – 4

Table 4.16 Light Fastness ratings of padded and baked samples for pigments derived from Acetoacetanilide

PIGMENTS	SUBSTRATE				
	COTTON	POLYESTER	WOOL	COTTON/POLYESTER	PAPER
B	5	4	4	4	5
E	4	5	5	5	5
H	4	4	5	4	4
K	4	4	4	4	4
M	3	3	3	3	3

Table 4.17 Wash fastness of resin-bonded and steamed samples of pigmemts derived from acetoacetanilide

PIGMENT	SUBSTRATE							
	COTTON		POLYESTER		WOOL		COTTON/POLYESTER	
	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE
B	3 – 4	3	2	2	3 – 4	3	3 – 4	3
E	4	3 – 4	3	3	4	3 – 4	4	3 – 4
H	3 – 4	4	4	3 – 4	4	3	4	3 – 4
K	3	2 – 3	3 – 4	3	3 – 4	3	3	3
M	2 – 3	2	3	2 – 3	3	2	3	2 – 3

Table 4.18 Wash fastness of resin-bonded and baked samples of pigments derived from acetoacetanilide

PIGMENT	SUBSTRATE							
	COTTON		POLYESTER		WOOL		COTTON/POLYESTER	
	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE
B	2-3	2-3	2	2	4	3-4	3	3
E	3	2-3	2	2-3	4	3-4	3	3-4
H	3	3	2	2	4	4	3	3-4
K	2-3	3	2	2-3	3	3-4	3	3
M	2	2 –3	2	2	2 –3	3	2 – 3	2

Table 4.19 Light fastness ratings of resin-bonded and steamed samples for pigments derived from acetoacetanilide

PIGMENT	SUBSTRATE				
	COTTON	POLYESTER	WOOL	COTTON/POLYESTER	PAPER
B	4-5	2	4-5	4	4
E	4	5	5	4-5	5
H	3	3	5	3	4
K	3	3-4	3-4	3	4
M	2	2-3	3	3	3

Table 4.20 Light fastness ratings of resin-bonded and baked samples for pigments derived from acetoacetanilide

PIGMENTS	SUBSTRATE				
	COTTON	POLYESTER	WOOL	COTTON/POLYESTER	PAPER
B	5	2 – 3	5	4 – 5	5
E	4	5 – 6	5 – 6	4 – 5	5
H	3 – 4	3	5	3	4
K	3	3 – 4	4	3	4 – 5
M	2 – 3	2 – 3	3	3	3

Table 4.21 Wash fastness of padded and steamed samples of pigments derived from acetoacet-2,5-dichloroaniline

PIGMENT	SUBSTRATE							
	COTTON		POLYESTER		WOOL		COTTON/POLYESTER	
	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE
C	4	4	4	4	3 – 4	4	4	4
F	4	4	4	4	4	4	3 – 4	3 – 4
I	3	3 – 4	3	3 – 4	3 – 4	4	4	4

Table 4.22 Wash fastness of padded and baked samples of pigments derived from acetoacet-2,5-dichloroaniline

PIGMENT	SUBSTRATE							
	COTTON		POLYESTER		WOOL		COTTON/POLYESTER	
	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE
C	4	3 – 4	4	3 – 4	4	3 – 4	4	4
F	3 – 4	4	4	4	4	4	4	3 – 4
I	3	3 – 4	3 – 4	3	3 – 4	4	3 – 4	3 – 4

Table 4.23 Light fastness ratings of padded and steamed samples for pigments derived from Acetoacet-2,5- dichloroaniline

PIGMENT	SUBSTRATE				
	COTTON	POLYESTER	WOOL	COTTON/POLYESTER	PAPER
C	4	3	5	3	4
F	5	4	4	4	4 - 5
I	4	4	4 – 5	5	5

Table 4.24 Light fastness ratings of padded and baked samples for pigments derived from acetoacet-2,5- dichloroaniline

PIGMENT	SUBSTRATE				
	COTTON	POLYESTER	WOOL	COTTON/POLYESTER	PAPER
C	5	3	5	4	4
F	4	5	4	4 – 5	5
I	4	4	5	5	5

Table 4.25 Wash fastness of resin-bonded and steamed samples of pigments derived from acetoacet-2, 5-dichloroaniline

PIGMENT	SUBSTRATE							
	COTTON		POLYESTER		WOOL		COTTON/POLYESTER	
	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE
C	3-4	3-4	4	4	3-4	4	4	4
F	3	3-4	3-4	4	4	4	3-4	3-4
I	3	4	3	3-4	3-4	4	4	4

Table 4.26 Wash fastness of resin-bonded and baked samples of pigments derived from acetoacet-2, 5-dichloroaniline

PIGMENT	SUBSTRATE							
	COTTON		POLYESTER		WOOL		COTTON/POLYESTER	
	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE	CHANGE IN COLOUR	STAINING OF WHITE
C	4	3-4	3-4	3	2	2-3	3	3
F	3-4	3	4	3-4	4	3-4	3-4	3
I	3-4	3	3-4	3	3	4	3-4	3-4

Table 4.27 Light fastness rating of resin-bonded and steamed samples for pigments derived from Acetoacet-2, 5-dichloroaniline

PIGMENT	SUBSTRATE				
	COTTON	POLYESTER	WOOL	COTTON/POLYESTER	PAPER
C	4	3	5	3	5
F	4 – 5	4 – 5	5	4 – 5	5
I	4	4 – 5	4 – 5	5	5

Table 4.28 Light fastness rating of resin-bonded and baked samples for pigments derived from Acetoacet-2, 5-dichloroaniline

PIGMENT	SUBSTRATE				
	COTTON	POLYESTER	WOOL	COTTON/POLYESTER	PAPER
C	4	3	5	3	4
F	5	4	4	4	4-5
I	4	4	4-5	5	5

The results of the wash fastness tests showed that pigments derived from β-naphthol generally give better wash fastness than those derived from either acetoacetanilide or acetoacet-2,5-dichloroaniline irrespective of the method of application and choice of substrate. Pigments derived from acetoacet-2, 5-dichloroaniline however, gave wash fastness better than those derived from acetoacetanilide in virtually all cases. This could be attributed to the presence of the two chlorine (halogen) atoms that facilitated better fastness.

From the tables the wash fastness properties of padded samples appeared better than those of the resin-bonded fabrics and most of the pigments showed poor wash fastness with the exception of pigment J which wash fastness showed average to good fastness properties on all the samples tested. This result is not surprising, because from Table 4.2 pigment J had the highest absorbance among the rest of the pigments, had narrower band and retained less in the fabric as a result of absence of salt-forming groups e.g. carboxylic (-COOH) acid, sulphonic acid (-SO_3H) group in its structure.

Generally, pigments C, D and F recorded better wash fastness properties on all tested substrates than the rest of the pigments. This may be partly due to their relatively high molecular weights compared to the rest of the pigments.

4.7 Light fastness properties

The results of the light fastness test are as summarized in Tables 4.7, 4.8, 4.11, 4.12, 4.15, 4.16, 4.19, 4.20, 4.23 4.24, 4.27 and 4.28.

As can be seen from the tables of light fastness ratings pigments A, D, G, B, E, H, C, F showed good light fastness properties and are better than those of pigments J, I, K and M. This may be attributed to the molecular structure of the pigments. On the whole, the light fastnesses of most of the synthesized pigments were better on cotton, wool, paper than on polyester or cotton/polyester.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

Conclusion

It was generally observed that variation of either the diazo or coupling component resulted in different pigments with different colours being produced, and absorbing at different wavelengths. The yield of the synthesized pigment is directly proportional to the quantity of the diazo or coupling component used as indicated. However the quantity of either the diazo or coupling component used for synthesis has no effect on the properties such as colour, melting point and fastness properties of the resultant pigment.

Reduction in the number and alteration in the positions of the nitro ($-NO_2$) groups substituted on the aromatic ring of the diazo component resulted in a decrease in absorbance depending on the type of coupling component used. It was however, observed that reduction in the number and alteration in the positions of the nitro ($-NO_2$) group while maintaining the same coupling component produced a bathochromic shift or effect. That means the number and position of the nitro group influenced the depth of shade or hue of the pigment. The same explanation accounts for the effect of methyl ($-CH_3$) group as a bathochrome in pigment J. The presence of two chlorine atoms in acetoacet-2,5-dichloroaniline has improved the colour (greenish-yellow) of pigments C, F and I as compared to pigments B, E, H, K and M (Yellow in colour) which were obtained based on acetoacetanilide only (without substituent) as coupling agent.

The incomplete recrystallisation of the pigments in some of the solvents used might mean that they had some slight impurities before their melting points were determined. However, the melting points obtained as shown in Table 4.1 gave strong indication that the level of purity of the pigments was high. The fact that the pigments have been successfully applied to 100% cotton, 100% polyester as well as paper shows that they can find suitable application on plastics/polymer, paper colouration and printing inks other than textile fibres. The padding method of application was found to be relatively better than the resin-bonded method as indicated by the results of wash fastness and light fastness ratings. This may be due to the effect of steaming and baking on the resin used. The effectiveness of the steaming and baking methods of fixation of the pigments was investigated. Both methods were found to be effective with the steaming method providing fairly better result. Generally the wash fastness properties of pigments obtained based on acetoacetanilide alone as coupling components are fair. This is largely due to the absence of colour-inducing substituent groups in its structure.

From the results of both wash and light fastness obtained it was observed that the pigments synthesized based on β-naphthol as coupling components were found to be better applied onto cotton, polyester and cotton/polyester (blend) while pigments obtained from both acetoacetanilide and acetoacet-2,5-dichloraniline are more useful on wool, paper and to a less extent polyester.

Recommendations

Several monoazo pigments have been synthesized in the past (Colour Index, 1982). and many more can still be synthesized depending on the availability and choice of the diazo components (arylamine) and the coupling components. This work was limited to monoazo pigments only. Disazo pigments should be synthesized and applied based on the same principle.

The five arylamine and three coupling components employed in this work are not exhaustive. Other diazo components such as 4-methyl-2-nitroaniline, 2-nitro-p-toluidine, 5-nitro-2-aminoanisole etc and coupling components such as pyrazolone should be tried with a view to producing pigments with greater molecular weight with high insolubility in organic media.

Numerous amounts of literature is available on the application of organic pigments (Christie, 1993), (Norbert, 1971). and requirements for achieving suitable properties during and after application. (Achi, 1985)' (Norbert, 1971), (Nkeonye, 1990).

The Padding and Resin-bonding methods of application were employed in this research work. It is recommended that the mass coloration technique of applying pigments should be applied to other substrates. In addition the suitability of the pigments for other end uses such as in paints should be investigated.

On general account the pigments had good fastness to washing while light fastness was only moderate.

In this regard, the fastness properties of these categories of pigments should further be investigated with a view to improving them.

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