Review Article: Pigments and Their Application as Pickering Emulsion Stabilizers

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ABSTRACT

Pigments are chemical compounds in the particulate form with colour imparting ability. The colour of pigments depends on their chemical structure. They are widely used as colourants by many industries in their formulation however it is sometimes not clear if the pigment particles reside at the interface or not. Coloured emulsions and foams are an essential class of dispersed systems where significant development is still needed, specifically in terms of different strategies to impart colour itself. Investigating the behaviour of pigment particles at fluid–fluid interfaces will help understand the microstructure of pigment-containing products. This is particularly important in an industrial context meaning that formulations containing pigments and interfaces may be simplified and possibly the colour of different products can easily be tuned to suit customer choice. In this review article, a brief account of pigment chemistry is provided, and a short literature review on pickering emulsions stabilized by pigment particles is given.

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1. Introduction

Pigments are colour imparting agents that exist in particulate forms that are not soluble in their medium of application. Their insolubilty is due to the inherent intermolecular aggregation through hydrogen bonding and van der Waals forces [1]. Their application properties depend on their insolubility in the pigmented medium. Pigments tend to absorb or emit light in the visible region. Absorption occurs when radiant energy is used to raise the molecules in a substance to a higher energy level. Scattering is the process by which light is re-directed in multiple directions because of refraction and reflection. The object will appear transparent if the process involves only absorption while the object will appear either translucent or opaque if scattering occurs [2]. When pigments absorb light of a specific wavelength (corresponding to a colour), its complementary colour will be observed as the colour of the pigment, i.e. colour corresponding to the wavelength of transmitted light.

Research studies investigating the optical properties of emulsion are rare, given its widespread occurrence in cosmetics, food, agrochemical, and pharmaceutical products. The colour of an emulsion depends on its interaction with light, and its inherent properties control this (e.g., drop size, concentration, and refractive index) and the presence of any colourant (e.g., a pigment).

In many applications, colour is usually introduced into a material by adding a pigment. Pigments are used extensively in many different products, including ink [3], cosmetics [4], surface coatings [5], paint, and in electronic devices for liquid crystal displays and electrostatically charged toners [6,7]. In most of these applications, the pigment particles are used in combination with other materials like polymers, surfactants, other particles, and solvents. However, it is unclear if the pigment particles reside at the interface. Apart from the traditional use of pigments as a colourant in many formulations, pigment particles can also stabilize emulsions of oil and water in the absence of other components. Implying that pigment particles may be surface-active in addition to being an ingredient imparting colour, enabling formulations containing pigments to be simplified. This article is meant to be a short review of the behaviour of pigment particles at oil--water interfaces. In this article, a brief description of pigment, various classes of pigment, and the relationship between the chemical structure and colour of pigment will be discussed. Lastly, a literature review on emulsions stabilized by organic and inorganic pigments is highlighted.

2. Pigments

Pigments of different colours exist, and the colour difference is due to the variation in the colour absorbing ability of each pigment, related to differences in their chemical structure [2]. Pigments usually exist in a crystalline form. Their crystal structures are formed during crystallization due to growth on nuclei of pigment particles or surfaces of foreign materials serving the same purpose. The nature of the nucleating agents influences the rate of crystallization and the pigment morphology. Pigments tend to form highly ordered crystalline structures by virtue of some structural features such as intermolecular hydrogen bonding, van der Waals interactions, and stacking between adjacent planar molecules [6,8].

Pigment particles can exist either as a single crystal (primary particles), aggregates, or agglomerates. The primary particles are the final crystals that make the crude pigment products, and they may assume a variety of shapes, such as cubes, platelets, needles, bars, or some irregular shapes. Particle aggregates are formed when the primary particles grow together at their surfaces. Dispersion processes do not easily break down aggregates. Their sum of the surfaces of individual particles is usually greater than the total surface area of an aggregate. Agglomerates are groups of single crystals or aggregates that are linked together at their corners and edges (but did not grow together), and dispersion processes can separate them. In an agglomerate, the total surface area may not be significantly different from the sum of the surface area of individual particles. The ability of

pigments to disperse in a liquid is primarily determined by the nature and density of the agglomerates, which in turn depends on particle shape and density [9].

The commercial performance of pigments in a pigmented system is moderated by a long list of its application properties, such as colouristic performance, rheological behaviour, durability, and ecological compatibility. From the end user's point of view, the pigment must fulfil specific requirements regarding such properties. The most fundamental performance criterion is their colour. The most desirable property is probably the value in use or colour value per kg of the pigment. The colour value usually translates into tinctorial strength and purity of shade, both of which depend on the absorption spectrum intrinsic to the pigment structure [10].

2.1. Relationship between chemical structure and colour of pigments

The study of the correlation between the chemical structure and colour of pigments began in the early days of dyestuff chemistry. The molecule of colourants contains a system of conjugated double bonds called chromophores that are responsible for their colour [11]. Examples of some organic colourants as well as their chromophoric groups are given in **Table 1**. A chromophore is a component of the pigment molecule where absorption takes place and a change in electron density during excitation processes. It is a region in a molecule where the change in energy between two distinct molecular orbitals falls within the visible region. A substance appears coloured when it absorbs light in the visible region (400–800 nm). This means that a chromophore may or may not give colour to a compound depending on the wavelength of absorbed radiation.

The overlapping of atomic orbitals forms molecular orbitals. The direct overlapping gives rise to sigma (δ) bonds, while the side-by-side overlapping of atomic orbital results in the formation of pi (π) bonds. Electronic transitions usually occur in molecules when an electron is promoted from an occupied π-orbital (ground state) to an empty antibonding pi-orbital (π^*) [12].

A molecule possessing carbon-carbon double bonds (C=C) or carbon-carbon triple bonds (C≡C) as a chromophore can undergo only $\pi \rightarrow \pi^*$ transition. In contrast, a compound containing chromophores like C=O, C≡N or N=N (i.e., possessing σ, π and nonbonding (n) electrons), transitions such as $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ are possible. The energy change (ΔE) during this electronic transition is given by Planck's equation [13].

$$\Delta E = h\nu = hc/\lambda \qquad (1)$$

where h is Planck's constant (J s), ν is the frequency of light (Hz), c is the velocity of light (m/s), and λ is the wavelength of the absorbed light (nm). This equation shows that the energy change associated with this transition is inversely related to the wavelength of the absorbed light. For instance, a yellow pigment that absorbs light of a short wavelength *(e.g.,* blue) needs higher excitation energy when compared to a red pigment that absorbs light of a long wavelength (bluish-green). The range of wavelengths, colour, and their corresponding complementary colour are given in **Table 2**.

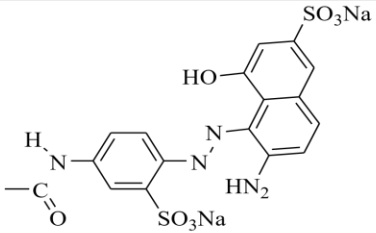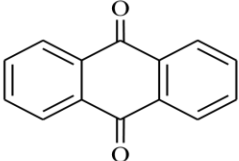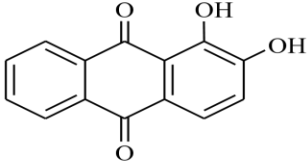**Table 1.** Some examples of the chromophore in organic colourants.
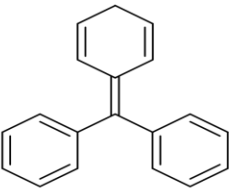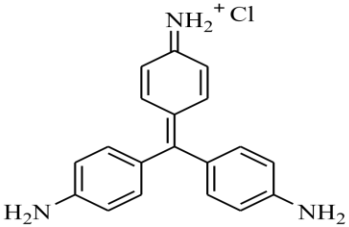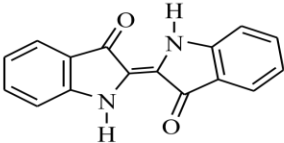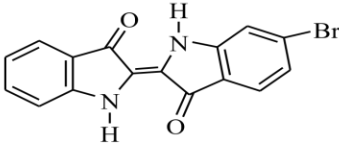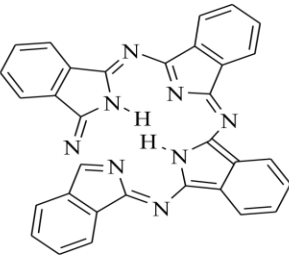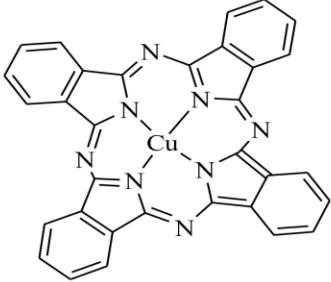
Chromophore Name	Chromophoric Group	Chemical Structure of Colourant
Azobenzene		
Anthraquinone		
Triarylmethane		
Indigo		
Phthalocyanine		

Table 2. Range of wavelengths, colour, and the corresponding complementary colour

Wavelength	Colour	Complementary Colour
400–435	Violet	Greenish-yellow
435–480	Blue	Yellow
480–490	Greenish-blue	Orange
490–500	Bluish-green	Red
500–560	Green	Purple
560–580	Yellowish-green	Violet
580–595	Yellow	Blue
595–605	Orange	Greenish-blue
605–750	Red	Bluish-green

An instrumental technique for characterizing the colour of pigments is called UV/visible spectroscopy. The colour of a substance in a solution can be related to its UV/visible spectrum by hue, intensity, and brightness. Hue is a property of a colour that enables it to be seen and determined at a particular dominant wavelength. A change in hue can be brought

about by a structural change in a pigment molecule. The brightness of a colour can be inferred from the shape of the absorption band. A narrow-shaped absorption band indicates that the colour of the colourant is bright, while a dull colour has a broad absorption band. The intensity of a colour can be related to the molar extinction coefficient at the maximum absorption wavelength, λ_{max}, and this can be obtained from the UV/visible spectrum through the application of Beer-Lambert's law,

$$A = -\log_{10} \frac{I}{I_0} = A = \varepsilon c l \qquad (2)$$

where I is the intensity of the transmitted light, Io is the intensity of the incident light, A is the absorbance, is the molar extinction coefficient (M^{-1} cm^{-1}), l is the path length (cm), and c is the concentration of the colourant (M). The intensity of a colour can also be related to the area under the absorption band. The intensity of pigment colour can be altered in the presence of certain substituents called auxochromes which are anchored to the system of conjugated double bonds [14]. They are called colour colour-enhancing groups. Auxochromes alone cannot show any absorption above 200 nm, and they cannot produce colour by themselves, but when present along with a chromophore in a molecule, they can intensify the colour of the pigment. A peculiar feature of auxochromes is that they possess at least a lone pair of electrons which is used for extending conjugation through resonance. The combination of a chromophore and auxochromes behaves as a new chromophore having different values of λ_{max} and εmax. For example, benzene shows λ_{max} = 256 nm and ε_{max} = 200 M^{-1} cm^{-1}, whereas phenol shows λ_{max} = 270 nm and ε_{max} = 1450 M^{-1} cm^{-1}. Pigments possessing similar structures and chromophoric groups do have extinction curves that look alike and the peak of maximum absorption. A shift in the position of absorption to a shorter wavelength is called a hypsochromic shift, while a shift to a longer wavelength is called a bathochromic shift [15].

2.2. Classification of pigments

Pigments can be classified into organic and inorganic. Organic pigments are made up of carbon and hydrogen and other elements like oxygen or nitrogen, while inorganic pigments are composed of mineral compounds.

2.2.1. Organic pigments

Organic pigments are made up of carbon chains and rings, while some pigments also contain metallic elements in their chemical structure, which help to stabilize the properties of the organic moiety in the pigment molecule. Their synthesis involves a series of chemical reactions. Organic pigments are produced from raw materials obtained from petrochemicals like benzene, toluene, xylene, naphthalene, and ethylene. These chemicals are used to make useful reactive intermediates (e.g., naphthalene sulphonic acid) which further react in a series of temperature- and pressure controlled processes to give the final organic pigment. After synthesizing organic pigments, they are subjected to further finishing or conditioning processes for the pigment to have the right chemical and physical properties required for specific end uses. Organic pigments can be classified according to their chemical nature or colour [16]. Based on their chemical nature, we have azo, phthalocyanine, carbonyl, and dioxazine organic pigments.

Azo pigments

Azo is the name for organic compounds containing a nitrogen-nitrogen double bond between two sp^2–hybridized carbon atoms [17]. They are structurally based on the general formula: −N=N−.

Most azo pigments are mono or diazo compounds. They constitute the largest group of organic pigments concerning both chemical structure and production volume because of easy accessibility to raw materials and an economical method of production. They exist in different colours, such as yellow, orange, red, pink, and brown. They are usually prepared through a coupling reaction performed on a small scale in the laboratory or on a large scale in an aqueous medium. Azo pigments are prepared by a reaction sequence of the diazotization and coupling involving a primary

aromatic amine and a nucleophilic aromatic or aliphatic compound with active methylene groups. The primary aromatic amine is called the diazo component, while the nucleophilic moiety is the coupling component. The diazo component can be a mono-, di-, or trisubstituted aniline, which can undergo a diazotization reaction [9,18]. Examples of diazo components are given in **Figure 1**. A reaction scheme for preparing a monoazo pigment is given in **Figure 2**.
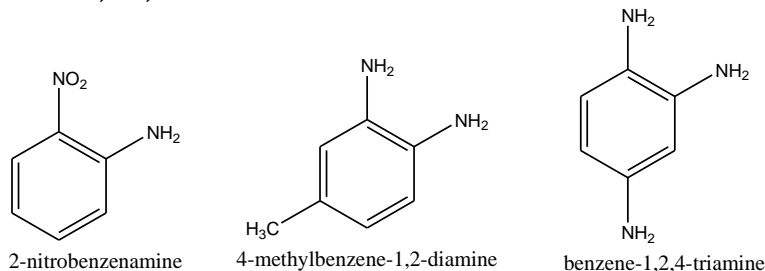

Figure 1. Some specific examples of diazo components

4-(2-Diazenylbenzenesulfonoyl)-3-hydroxynaphthalene-2-carboxylic acid
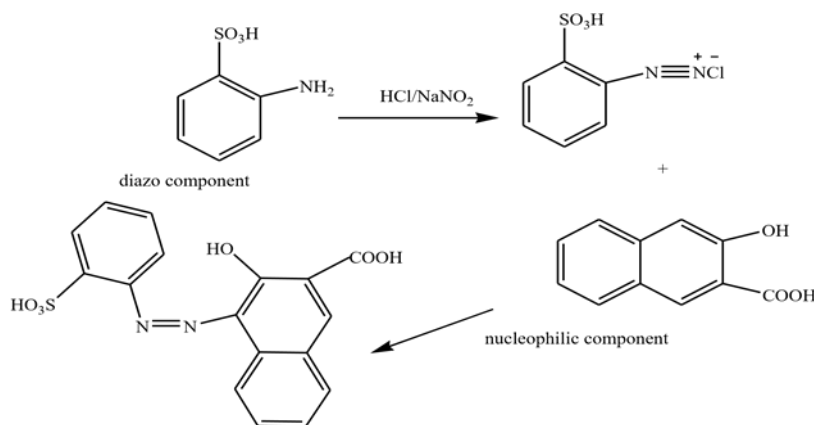
Figure 2. Reaction scheme for the formation of a monoazo pigment

Some specific examples of organic pigments with the azo chromophore are β-naphthol pigments, Naphthol AS, benzimidazolones, and azo pigment lakes. Monoazo pigments provide shades ranging from greenish-yellow to deep reddish yellow or orange. However, due to their poor fastness properties, their application has been limited, and this has reduced their commercial importance because of the advent of alternative structures with excellent fastness properties. The β-naphthol pigment contains 2-hydroxynaphthalene (β-naphthol) as the nucleophilic coupling component. Their shades fall within the yellowish-orange to the bluish-red range. They exhibit poor fastness properties to organic solvents and are used mainly in air-drying paints. Naphthol AS, also known as Naphthol Red is an azo organic pigment which that is used extensively for coating and painting. It provides shades ranging from yellowish to very bluish red. They are monoazo pigments containing an aromatic amide of 2-hydroxy-3-naphthoic acid as a coupling component (**Figure 3**). These pigments are used in the production of printing ink.9
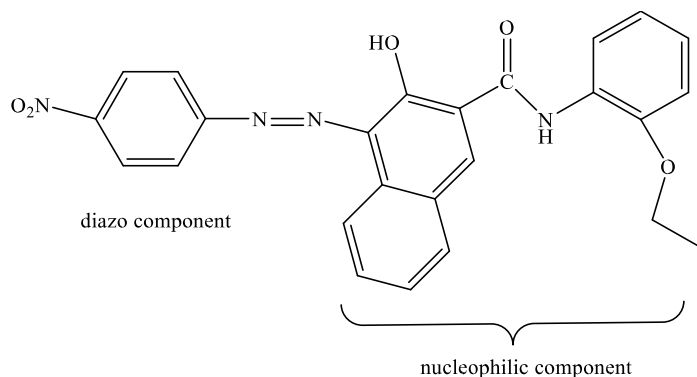
Figure 3. Chemical structure of Naphthol Red (Pigment Red 170)

Benzimidazolone pigments are azo pigments containing the 5-aminocarbonyl benzimidazolone group as the nucleophilic component. A good example is pigment yellow 151 (**Figure 4**). This class of pigment covers the entire range of shades in the red and brown parts of the visible spectrum.
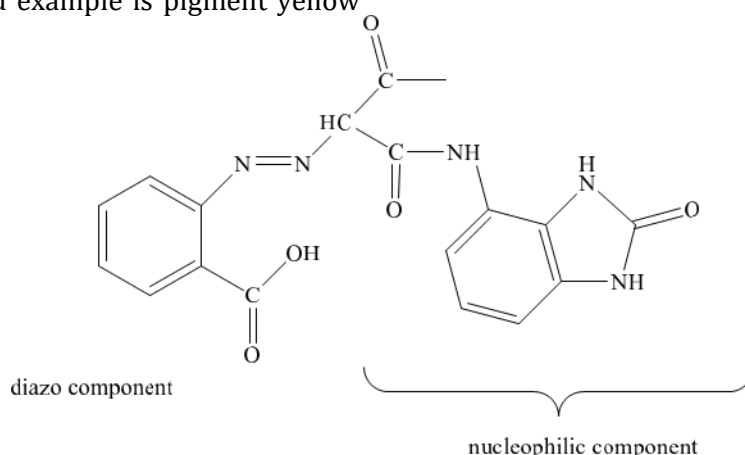

Figure 4. Chemical structure of benzimidazolone pigment

Azo pigment lakes are colourants bearing sulphonic and/or carboxylic groups used as pigments after being rendered insoluble by conversion into insoluble alkaline earth or manganese salts. Depending on the coupling component, there are four industrially essential pigments in this class: namely β-naphthol, 2-hydroxy-3-naphthoic acid, Naphthol AS derivatives, and naphthalene sulphonic acid derivatives. These pigments exhibit good fastness properties, making them suitable candidates for producing printing inks. They are also used as colourants in the plastics and paint industries. Because of their salt character, this class of pigment is faster to solvents and more resistant to migration than the corresponding azo pigments. This property also makes them have excellent thermal stability.9 The structure of an azo pigment lake containing barium is shown in **Figure 5**.
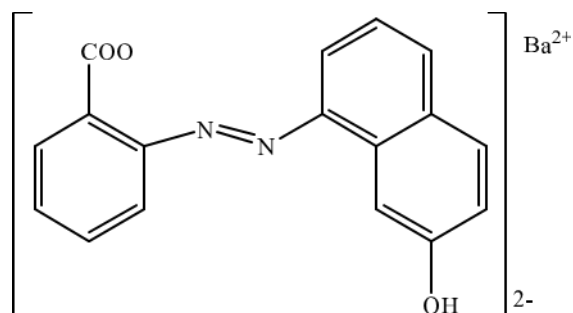
Figure 5. Chemical structure of β-naphthol pigment lake

Phthalocyanine pigments

These are pigments derived from the phthalocyanine structure. Phthalocyanine is a macrocyclic aromatic compound with a network of −C=N− bonds. The phthalocyanine system may be considered as a derivative of tetrabenzoporphyrin. It is a planar molecule consisting of four isoindole units connected by four nitrogen atoms to form together an internal 16-membered ring of alternate carbon and nitrogen atoms [19]. This molecule can chelate with a variety of metals. The copper (II) complex of phthalocyanine is used as a pigment. The chemical as well as the physical properties of phthalocyanine pigments, makes them an essential organic pigment in the market today. The structure of copper phthalocyanine pigment is shown in **Figure 6**.
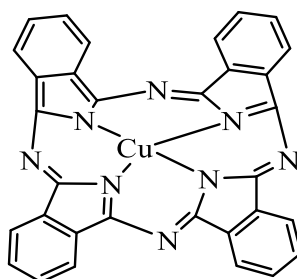
Figure 6. Chemical structure of copper phthalocyanine pigment

The presence of pi electrons in the perimeter of their molecules makes the phthalocyanine pigments aromatic compounds. The light absorption ability of the pigment depends on the nature of the central metal atom, the substituent pattern on the outer rings, and the degree of pi-electrons delocalization within the ring [19]. The phthalocyanine pigments are exceptionally stable compared to most synthetic organic colourants. Phthalocyanine pigments can be synthesized by heating phthalic acid derivatives with a nitrogen-containing functional group. A suitable precursor of a phthalocyanine pigment is phthalonitrile. This reaction can be catalyzed in the presence of metallic salts [20–22]. This pigment can also be prepared by heating phthalic anhydride with urea, copper (I) chloride, and a catalytic amount of ammonium molybdate in a high boiling solvent. A schematic illustration of the synthesis of a phthalocyanine pigment is shown in **Figure 7**. The intermediate formed during the reaction sequence undergoes a tetramerization with a cyclization aided by the presence of copper ion to form copper phthalocyanine. Halogenation of copper phthalocyanine produces a green colour pigment which is an essential class of organic pigments used for coatings, making inks, and plastics. The vital electronegative chlorine atoms influence the distribution of electrons in the phthalocyanine structure, thus shifting its absorption spectrum. Copper phthalocyanine, like many other phthalocyanines, is polymorphous. The reddish-blue α-form is metastable and is readily converted into the stable, greener shade β-form [16].
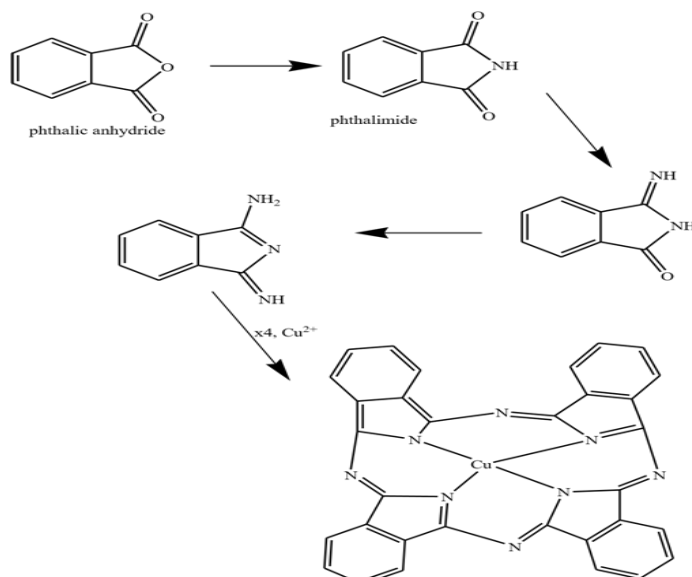
Figure 7. Reaction scheme for the synthesis of copper phthalocyanine pigment

Carbonyl pigment

The chemical class of organic pigments which is second in importance to azo pigments is the carbonyl pigment [11]. The pigment contains the carbonyl functional group (C=O) as the essential chromophoric unit. Most of the carbonyl pigments contain two or more carbonyl groups, and these electron-withdrawing groups have the potential to provide a wide range of colours that spread across the visible spectrum. More importantly, the carbonyl pigments can provide absorption bands having a long wavelength with a system of short conjugated bonds. They usually contain an organic moiety such as quinoid or indigoid structures with two conjugated C=O groups in a carbocyclic ring or heterocyclic rings containing either N-, S-, or O- atoms. Carbonyl pigments are numerous, and they include quinacridones, diketopyrrolopyrroles, perylenes and anthraquinones pigments. Their molecular geometry allows them to undergo multiple intra- and intermolecular hydrogen bonding and/or stacking, which account for their insolubility and thermal stability. Carbonyl pigments can be prepared by a condensation reaction [23].

One of the most crucial chromophoric systems developed for pigment applications is quinacridone. It is a pigment containing alternate fused benzene and 4-pyridone rings. Different numbers of geometrical arrangements are possible for these pigments. However, the pigment exhibits outstanding technical properties, which displays the linear *trans* arrangement. The structure of a quinacridone pigment is given in **Figure 8**. Quinacridones are polymorphous, and this characteristic has a significant effect on their colour. For example, the pigment shown in **Figure 8** exists in three different polymorphic modifications, each one with its own distinct X-ray powder diffraction characteristic pattern. The α- and β-polymorphs are red, whereas the γ-form is violet.
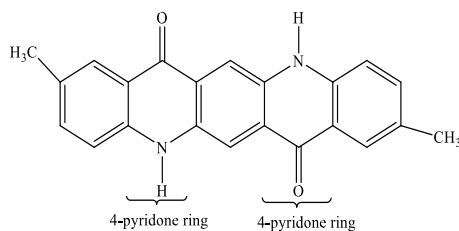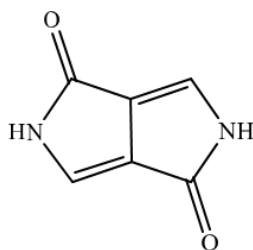

Figure 8. Chemical structure of quinacridone

Another type of carbonyl pigment is diketopyrrolopyrroles. These pigments are based on the 1,4-diketopyrrolo[3,4-*c*]pyrrole system [19]. The chemical structure of 1,4-diketopyrrolo [3,4*c*]pyrrole is shown in **Figure 9.**
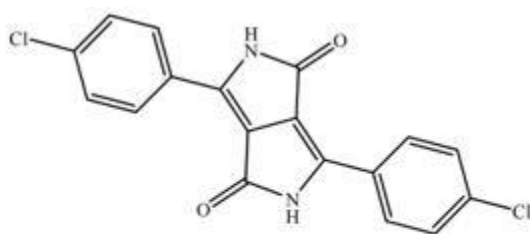

2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione
Figure 9. Chemical structure of diketopyrrolopyrrole

Pigment Red 254 is an example of diketopyrrolopyrrole pigments which is commercially relevant (**Figure 10**). It contains two fused five-membered ketopyrrole rings, and by incorporating appropriate substituents into its molecular structure, they can provide shades ranging from orange through red to bluish-violet. This pigment also shows excellent fastness properties from small molecules like the quinacridones [19].

3,6-bis(4-chlorophenyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione

Figure 10. Chemical structure of Pigment Red 254

Perylene pigment is another carbonyl pigment type that contains perylene as the main chromophoric group. Perylene is a polycyclic aromatic compound occurring as a brown solid. Some high-grade perylene pigments, mostly primarily red but also including black, are of industrial importance. An example of the perylene pigment is shown in **Figure 11**. An interesting observation in the perylene series is that small structural changes in the side-chain can lead to profound colour differences [19].
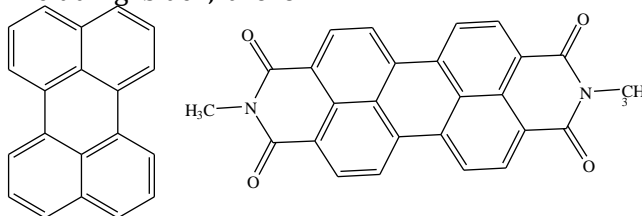
Figure 11. Chemical structure of (**a**) perylene and (**b**) perylene pigment

Dioxazine pigments

Oxazines are heterocyclic organic compounds containing carbon, oxygen, and nitrogen atoms in a doubly unsaturated six-membered heterocyclic ring. They do exhibit isomerism depending on the relative position of the double bonds and heteroatoms. The different possible isomeric forms of oxazines are shown in **Figure 12**. Dioxazine pigments, as the name implies, contain two oxazine rings as the chromophoric group. They are not numerous, and their shade

is generally restricted to violet and blue. A typical example of dioxazine is Pigment Violet 23, and the chemical structure is shown in **Figure 13**. This pigment has a brilliant, intense

reddish violet colour. It has an excellent light fastness property and heat and solvent resistance [19].
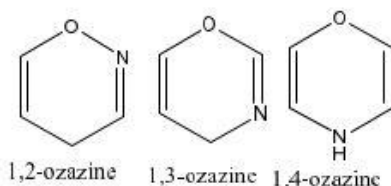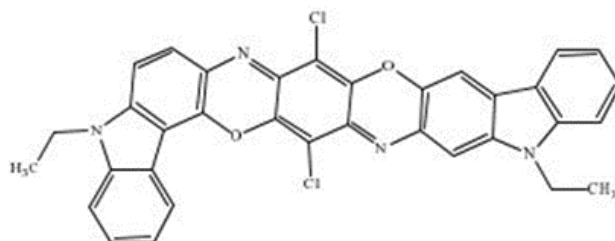

Figure 12. Various isomeric forms of oxazines

Figure 13. Chemical structure of Pigment Violet 23

2.2.2. Inorganic pigments

Inorganic pigments are basically mineral oxides or sulphides of one or more metals [23]. Some inorganic pigments have limited use due to toxic heavy metals in their chemical structure, which cause environmental problems. For example, cadmium pigments have been almost phased out due to their high toxicity. Inorganic pigments are numerous and they are about 95 percent of total pigment. They can be classified into white, coloured and black inorganic pigments [24]. White pigments do not absorb light in the visible region (wavelength 400–800 nm) but scatter incident radiation in this region as completely as possible. The optical properties of white pigments are due to their low light-absorbing ability in the visible region and their strong, non-selective light scattering ability. An example of white inorganic pigments is titania. It is the naturally occurring oxide of titanium with the chemical formula TiO_2.

The optical properties of coloured inorganic pigments are controlled by selective light absorption and, to a large extent, by a selective light scattering ability. The non-selective

absorption of light primarily causes the optical effect of black pigments. Examples of coloured inorganic pigments are iron oxide red, yellow cadmium pigments, ultramarine pigments, chrome yellow, and cobalt blue. Examples of black inorganic pigment are carbon black and iron oxide black. Carbon black is a material produced by the incomplete combustion of heavy petroleum products such as tar, coal tar, etc [25].

2.2.3 Pigment-stabilized emulsions

Emulsions are a class of dispersed systems consisting of two immiscible liquids in which one of the liquid is dispersed as liquid droplets in the other liquid called the continuous phase [26]. The formation of kinetically stable emulsions required the right composition in the formulation. Thus, the formation of emulsions with long shelf-lives is of increasing interest given their occurrence in many processes related to the food [27], cosmetics [28], and pharmaceutical industries [29]. The area of particle-stabilized emulsions is fast growing and very topical at present both in the academic and

industrial sectors. This is where traditional emulsifiers of surfactant or polymer molecules are replaced by solid particles, which, by virtue of their irreversible adsorption, confer exceptional stability to droplets against coalescence. The stabilization of emulsions against coalescence is achieved by the accumulation of solid particles at the oil–water interface [30-32]. The structure of particle-stabilized emulsions is illustrated in **Figure 14a**. Colloidal particles of intermediate wettability can adsorb to oil–water interfaces and, therefore, stabilize an emulsion. The type of emulsion thus formed is usually determined by the particle wettability which is quantified by

the oil–-water contact angle, θ. For hydrophilic particles, θ measured into the aqueous phase is < 90° and produced oil-in-water emulsions. For hydrophobic particles, θ is greater than 90° and water-in-oil emulsions are preferentially formed [33–37]. The conversion from o/w to w/o emulsions and *vice versa* can be achieved either by varying the water volume fraction (catastrophic phase inversion) [38] or by changing properties that affect the particle wettability (transitional phase inversion) [39]. Phase inversion is a phenomenon in emulsion science whereby the dispersed phase suddenly becomes the continuous phase (**Figure 14b**).
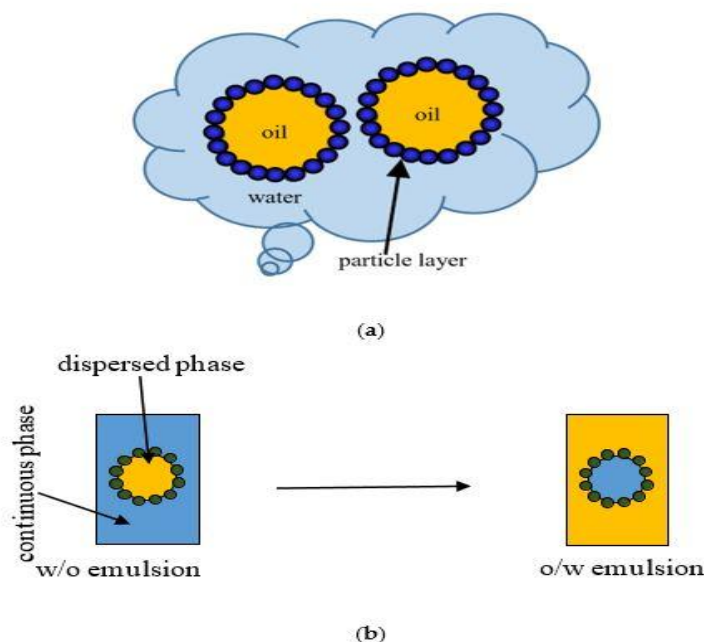

Figure 14. Schematic diagram illustrating (**a**) the structure of particle-stabilized emulsions (**b**) phase inversion

Traditionally, pigments are used in many industrial applications as colour imparting agents, but little is known about their emulsifying ability. Reports describing emulsion stabilization by inorganic pigments and carbon are available in the literature. Different types of black particles of carbon have been used as sole emulsifiers, and these include lamp black [40], carbon black [41], and carbon nanotubes [42]. Emulsions stabilized by so-called amphiphilic carbon nanotubes were described by Wang and

Hobbie [43]. They provide evidence for single-walled carbon nanotubes (SWNTs) acting as a natural "surfactant" or interfacial material in macroscopic emulsions of water droplets in toluene. The microscopic images of water droplets in toluene obtained at different SWNT/water mass ratios show that the water droplets are spherical, polydisperse, and flocculated (**Figure 15**). Droplets with small sizes are obtained at higher SWNT/water mass ratios.
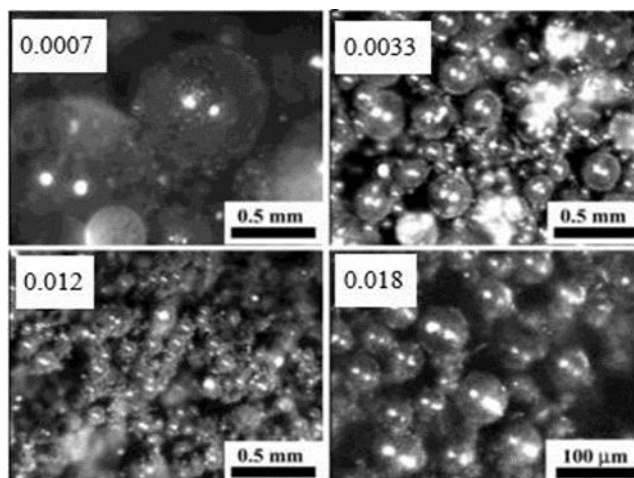
Figure 15. Optical micrographs of water-in-toluene emulsions prepared at different SWNT/water mass ratios. Reprinted from ref 43 with permission from *Langmuir* **2003**, 18, 3091. Copyright (2003) America Chemical Society

Modified carbon nanotubes have also been used as emulsifiers of water and cyclohexane [44]. These carbon nanotubes (CNTs) were rendered more hydrophilic by introducing some polar functional groups such as hydroxyl and carboxyl groups on the particle surface by oxygen plasma treatment, thus making it possible for the CNTs particles to form stable o/w emulsions. The effect of increasing the concentration of CNTs on the droplets morphology was studied. Bigger droplets were seen in cyclohexane-water emulsions prepared at low particle concentrations, whereas droplets with relatively small sizes were formed at high concentrations (**Figure 16**).
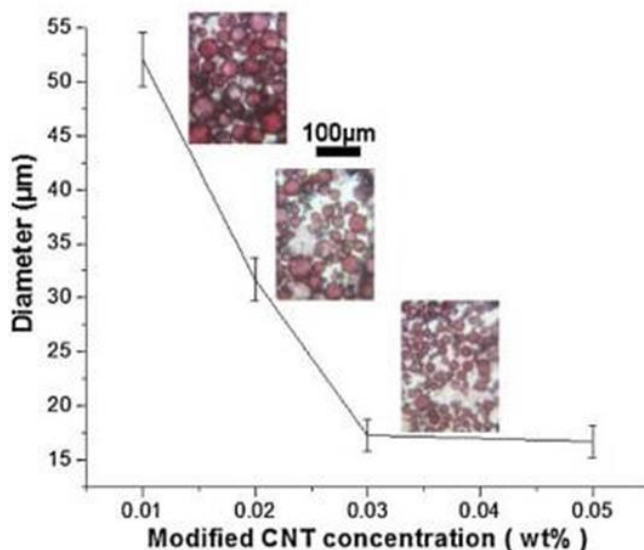

Figure 16. Variation of oil droplet diameter as a function of the concentration of plasma-treated CNTs. Reprinted from *J. Ind Eng. Chem.* **2011**, 17, 455. Copyright (2011) with permission from Elsevier

Particle-stabilised or Pickering emulsions have recently been prepared using multi-wall carbon nanotubes (MWNTs) [45, 46]. The carbon nanotubes exhibit surface activity at the interface in systems containing oil and water mixtures. In this context, Briggs *et al.* [47] used four different MWNTs obtained by modifying the surface of the MWNTs through covalent or non-covalent methods. Thus, the hydrophobicity of the multi-wall carbon nanoparticles (MWNTs) was changed, enabling the same particle to stabilize both types of emulsion. Emulsion phase inversion from w/o to o/w was induced by using particles of increasing hydrophobicity. The

interfacial thickness of the MWNTs was studied using transmittance electron microscopy. A coherent layer of MWNTs nanoparticles was observed at the interface, providing mechanical support against the coalescence of emulsion droplets (**Figure 17**).
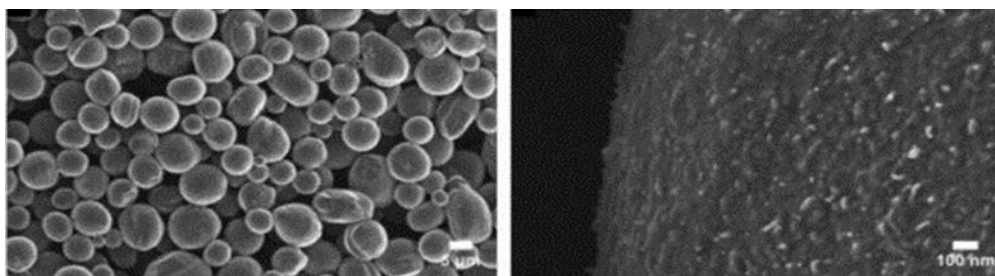

Figure 17. SEM images at different magnifications of the Pickering emulsion stabilized by 0.2 wt % of oxidized MWNTs. Reprinted from ref 47 with permission from *Langmuir* **2015**, 31, 13077. Copyright (2015) America Chemical Society

For both paraffin wax/water and dodecane/water systems, the thickness of the layer of MWNTs at the interface and resulting emulsion stability are shown to vary significantly with the approach used to modify the MWNTs. As the concentration of the nanotubes at the oil–water interface was increased, the emulsion stability was also enhanced. By measuring the interfacial thickness at different positions from TEM images, an average interfacial thickness of 75 nm for OxMWNT, 54 nm for AG-MWNT, and 107 nm for HEC-MWNTs was obtained. In a similar report from Bornaee *et al.* [48], functionalized multi-wall carbon nanotube was used to prepare oil-in-water emulsion. The influence of different cations on the properties of the resulting emulsions was studied. They found that bivalent cations greatly influenced particle wettability more than the univalent cation. Briggs *et al.* [49] have also studied the properties Pickering emulsions stabilized by mixtures of MWNTs of different wettability. They showed that transitional phase inversion was possible for emulsions of equal volumes of oil and water stabilized by a mixture of multiwalled carbon nanotubes of different wettability at varying weight fractions of hydrophobic particles but at fixed total particle concentration. The phase inversion occurred around a weight fraction of 0.94 (hydrophobic particles). The Emulsion droplet varies parabolically by decreasing in a fraction of hydrophobic MWNTs, with the particle mixtures stabilizing the smallest emulsion droplets. In contrast, larger droplets are formed by the more hydrophilic or hydrophobic MWNTs (**Figure 18**).
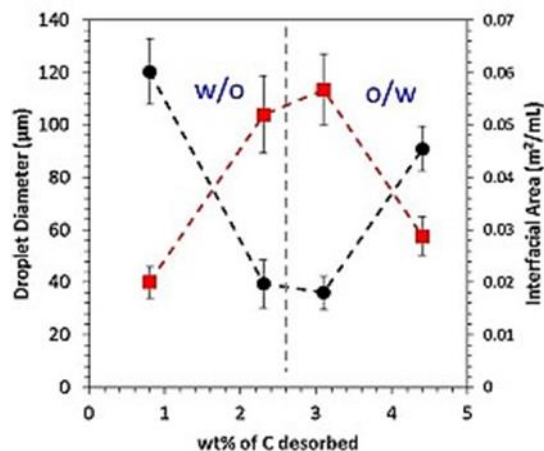

Figure 18. Variation of droplet diameter and interfacial area as a function of MWNT wettability when MWNTs are dispersed in water. Reprinted from *Colloids Surf. A* **2018**, 537, 227. Copyright (2018) with permission from Elsevier

Recently, Pickering emulsions stabilized by graphene oxide (GO) were reported by He *et al.* [50]. The influence of some parameters like oil type, sonication time, GO concentration, oil/water ratio, and pH on the properties of the emulsions was investigated. The influence of salt on emulsion formation and stability was studied. The microstructure of the emulsions stabilized by GO varies significantly with oil/water ratios. The formation of water-in-oil-in-water multiple emulsions was observed at high oil/water ratios (**Figure 19**). Also, Pickering emulsions stabilized by modified graphene oxides have been studied by Fei *et al.* [51]. The graphene oxide (AmGO) surface was modified using primary amines with different chain lengths. The modified graphene oxide formed a water-in-oil emulsion type. The correlation between emulsion properties and the alkyl chain length and alkyl chain content was studied. The emulsions with long-term stability were produced by AmGO within a wide range of pH (1 to 13) and salt concentrations (0.1 to 1000 mM). Also, the possibility of using the water-in-oil emulsions stabilized by AmGO for making supercapacitor was investigated.
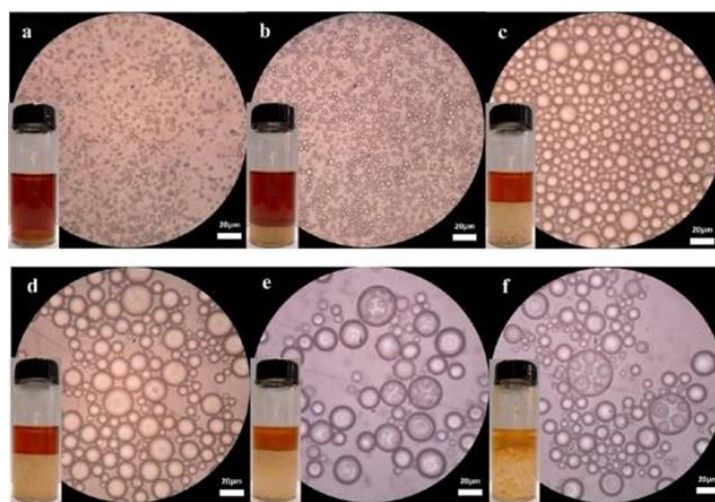

Figure 19. Optical images plus photos after 72 h of o/w emulsions stabilized by GO at different oil/water ratios: (**a**) 0.1, (**b**) 0.2, (**c**) 0.4, (**d**) 0.5, (**e**) 0.6 and (**f**) 0.8. Reprinted from ref 50 with permission from *ACS Appl. Mater. Interfaces* **2013**, 5, 4843. Copyright (2013) America Chemical Society

White particles of titania, when suitably chemically modified, were shown to be effective emulsifiers of oil and water [52,53]. Stiller *et al.* [52] showed that the properties of the emulsions depend on the hydrophobicity of the titania nanoparticles. Particle hydrophobicity depends on the inorganic and organic chemical reagents used to modify the titania nanoparticles. By fixing the particle concentration at 5 wt. %, catastrophic phase inversion of the emulsion was effected upon varying the water volume fraction from 0.2 to 0.8. Using equal volumes of oil and water, evidence for transitional phase inversion of emulsion as a function of particle wettability was also presented.

The stabilization of emulsion with brown microparticles of carbonyl iron [54] or iron nanoparticles [55] has been reported in recent times. In a report from Zhou *et al.* [56], hydrophilic Fe_3O_4 nanoparticles were used to prepare stable dodecane-water and silicone-water emulsions, but failed to stabilize butylbutyrate-water and decanol-water mixtures with macroscopic phase separation occurring after emulsification (**Figure 20**). Emulsions are oil-in-water for both dodecane and silicone oil. It was observed that not all of the particles adsorbed to drop surface to form stable emulsions. The fraction of adsorbed particles decreases with an increase in the initial oil volume fraction. Varying the particle concentration has no obvious influence on the stability of these emulsions, although the droplet size decreases with increasing particle concentration. The average droplet size increases with an increase in the oil volume fraction.
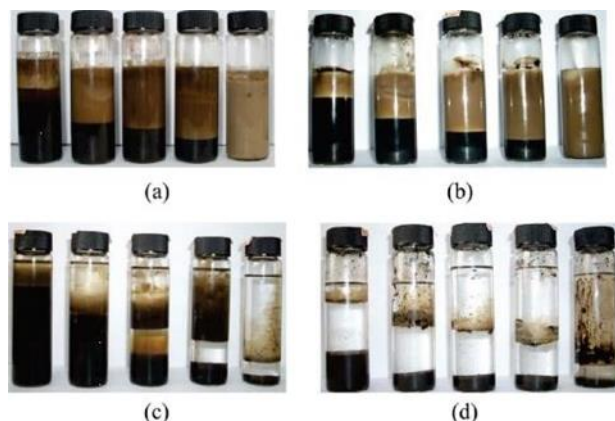
Figure 20. Photos after 20 days of vessels containing o/w emulsions stabilized by 1 wt.% Fe3O4 nanoparticle at different oil/water ratios (0.2, 0.4, 0.5, 0.6, and 0.8) for: (**a**) dodecane, (**b**) 10 mPa s PDMS, (**c**) butyl butyrate, and (**d**) decanol. Reprinted from ref 56 with permission from *Langmuir* **2011**, 27, 3308. Copyright (2011) America Chemical Society

The possibility of forming stable emulsions from the mixture of water and non-polar alkane using coloured organic pigment particles as an emulsifier has been demonstrated by Binks and Olusanya [57]. Seven organic pigments with the primary colours of the rainbow were used (pigment red, PR; pigment orange, PO; pigment yellow, PY; pigment green, PG; pigment blue, PB; pigment indigo, PI and pigment violet, PV). Pigments PR and PO are mono-azo pigments; PY is a quinophthalone while PG and PB belong to the phthalocyanine class. PI is a dioxazine pigment and PV is a quinacridone pigment. The chemical structures of the organic pigments are given in ref. 57. The suitability of these pigments as an emulsifier was first established using different characterization methods. The molecular solubility of the pigments in water or *n*-heptane was determined by a spectrophotometric method. Emulsions were prepared using the powdered particle method. With equal volumes of oil and water, preferred emulsions were w/o for six pigment types and o/w for PO (**Figure 21**). The type agrees with the measured oil–water contact angles.

Figure 21. Photo of preferred emulsions prepared using 1 wt. % particles for the seven pigments with ϕ_w = 0.5. Emulsions are w/o except those of PO which are o/w. Reproduced from ref 57 with permission from The Royal Society of Chemistry

The influence of pigment particle concentration was investigated on the stability and droplet size of the emulsions. The limited coalescence theory estimates the fraction of the droplet surface covered by the pigment particles. Pigment particles coating the droplet surface are evident in the optical microscopic images. Particle aggregates are seen on the surface of some emulsion droplets (**Figure 22**). At constant particle concentration, the influence of water volume fraction (ϕ_w) on the type and stability of emulsion was studied. For the most hydrophilic orange pigment (PO), emulsions are o/w at all ϕ_w, whereas they are w/o for the most hydrophobic pigments (red, yellow, green, and blue). Interestingly, the water volume fraction increases, two pigments stabilized emulsions (PI and PV) phase invert from w/o to o/w emulsions. The emulsion type is related to the pigment surface energy. For a high surface,

energy particle (PO) prefers o/w emulsions, while the low surface energy pigments (PR, PY, PG, and PB) prefer w/o emulsions at all water volume fractions. Pigments (PI and PV) of the intermediate surface energy phase invert from w/o to o/w emulsions upon increasing the water volume fraction.
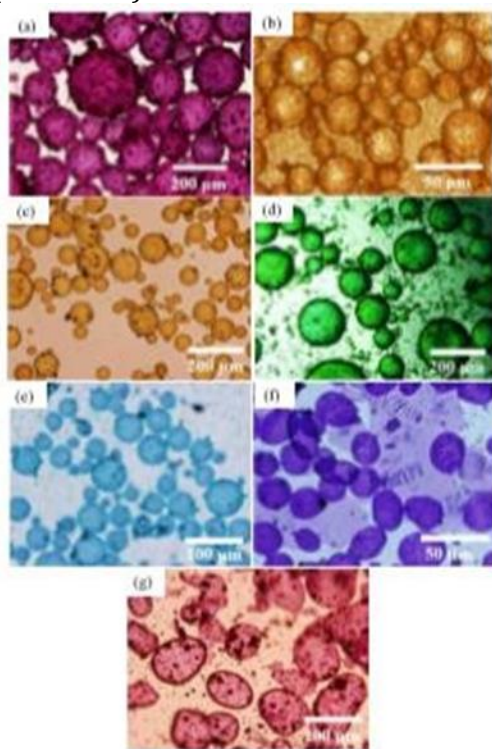

Figure 22. Optical images of preferred emulsions (ϕ_w = 0.5) stabilizd by 1 wt.% particles for (**a**) PR, (**b**) PO, (**c**) PY, (**d**) PG, (**e**) PB, (**f**) PI, (**g**) PV. Emulsions are w/o except those of PO which are o/w. Reproduced from ref 57 with permission from The Royal Society of Chemistry

Pickering emulsions stabilized by a mixture of coloured organic pigment particles have been investigated using equal volumes of water and *n*-heptane [58]. At fixed total particle concentration (1 wt.%), transitional phase inversion of emulsions from w/o to o/w occurs on increasing the weight fraction (wPO) of hydrophilic pigment, PO (**Figure 23**). The change in behaviour of emulsions takes place at different weight fractions of PO depending on the nature of the hydrophobic pigment used in the formulation. Interestingly, in the case of POPR and POPI particle mixtures, a distinct change in colour of the resulting emulsions appears around phase inversion. It was found that both pigment particles used in these formulations are situated at the interface, forming emulsions that are stable to coalescence. Preferred droplet sizes for both w/o and o/w emulsions increase towards phase inversion in line with an increase in the extent of sedimentation or creaming, respectively.

Figure 23. Photos of *n*-heptane-water emulsions (ϕ_w = 0.5) stabilized by a mixture of organic pigment particles at varying wPO for **(a)** POPR, **(b)** POPY, **(c)** POPI and **(d)** POPB. Reprinted from ref 58 with permission from *Langmuir* **2018**, 34, 5040. Copyright (2018) America Chemical Society

It is observed that most of the emulsions stabilized by the pigment particle mixture formed droplets with spherical morphology at all weight fractions of PO except system containing POPI which formed non-spherical droplets at low wPO values [58]. The organization of particles at droplet surface was probed by cryo-SEM analysis. For o/w emulsions, sublimation was used to remove the frozen oil leaving behind a cavity. In w/o emulsions, the particles at the interface was exposed by sublimation of frozen oil. The arrangement of particles at drop interfaces differs depending on emulsion type (**Figure 24**).

For w/o emulsions, particles are invariably close-packed and form a coherent layer between water and oil. By contrast, for o/w emulsions, particles form a network with bare areas within which are not occupied by particles. Particles in these interfaces are likely more charged, and repulsion between clusters of particles occurs. Reports highlighting interfacial particle clusters separated by a bare area at the droplet surface are common in the literature. A similar observation was reported by Tarimala *et al.* [59] for poly(dimethylsiloxane)in-water emulsions stabilized by polystyrene particles. At the oil–water interface, particles form small patches
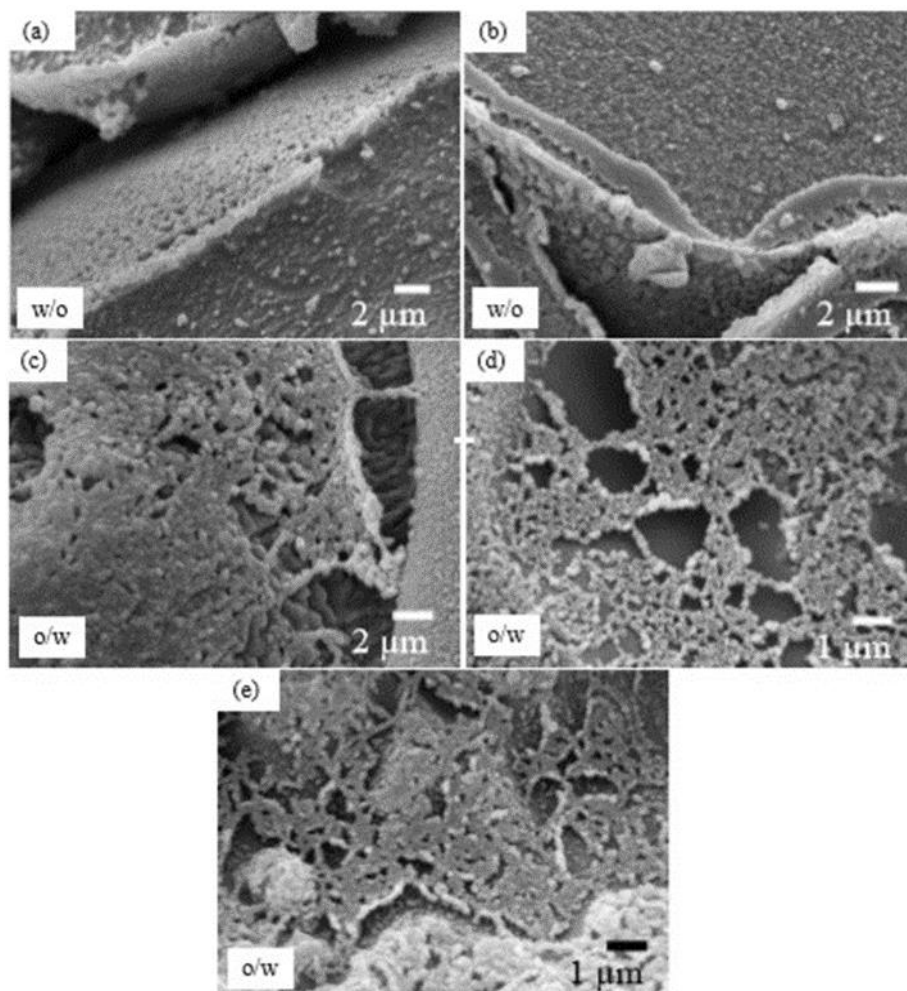
Figure 24. Cryo-SEM images of the surface of w/o emulsions for (**a**) POPY (wPO = 0.3) and (**b**) POPI (wPO = 0.2) and of o/w emulsions for (**c**) POPR (wPO = 0.5), (**d**) POPY (wPO = 0.6) and (**e**) POPB (wPO = 0.7) [58]..

with local hexagonal order; these domains were separated by other particle-free domains, and this was attributed to electrostatic repulsion between the charged particles at the oil–water interface.

3. Conclusion

Pigments of different colours exist, and the colour difference is due to the variation in the colour absorbing ability of each pigment, related to differences in their chemical structure. Pigments are classified into organic and in organic pigments. Organic pigments are made up of carbon chains and rings. At the same time, some pigments also contain metallic elements in their chemical structure, which help to stabilize the properties of the organic moiety in the pigment molecule. Inorganic pigments are basically mineral oxides or sulphides of one or more metals. Traditionally, pigments are used in many industrial applications as colour imparting agents, but little is known about their emulsifying ability. Coloured emulsions and foams are an essential class of dispersed systems where a significant development is still needed, specifically in terms of different strategies to impart colour itself. The physical appearance of emulsion-based products is of concern to most manufacturers because it is the most quickly identifiable quality responsible for the acceptance or rejection of a product. All other things being equal, consumers will prefer to buy what looks best. Hence, the ability of manufacturers to formulate emulsion-based products with admirable and reproducible colour depends on their in-depth knowledge of how the optical properties are related to the

composition and microstructure of their products.

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