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Nano-Pigments: Applications and Ecological Impact: A Review

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***Abstract* - Pigments are insoluble compounds that provide colours to the materials they are used in (e.g. paints, inks, cosmetics, etc.). These days, technology is shifting towards identifying, developing, and applying the use of nanomaterials, including the use of nano-pigments. Nano-pigments are pigments having particle sizes ranging from 1 to 100 nano metres (nm). However, recently the application of nano-pigments proved to be a boon for chemical industries. There will be a discussion over different kinds of pigments – inorganic as well as organic. The paper will focus on the comparison of Nano-pigments over the use of conventional micro-sized pigments. The main applications of pigments and the impact of nano-pigments will also be discussed. Additionally, there will be an overview of some nano-pigments, their syntheses, and applications. There will be a focus on the health and environmental impact of nano particles and nano pigments, with a discussion over the Environmental Guidelines.**

Keywords: Nanomaterials, nano-pigments, nanoparticles, pigments, dyes, ecology.

I. INTRODUCTION

One of the wonders which Mother Nature gave us humans is to see different shades of colour. It gives us an opportunity to see the beauty of our surroundings or to make any object beautiful. A colour additive is a substance which gives a colour to a given substrate when added. Plants, creatures, and minerals have been utilized as essential hotspots for colorants, colours or dyes since old times. Pigments are the most important substances used to add or change the colour of any substance.[1]

Pigments are insoluble materials utilized as colloidal scatterings. Dyes are dissolvable coloured substances - they are used in some areas such as staining wood furniture, colouring textiles, etc. Colour pigments are sometimes referred to as lakes and toners. Lake is originally a dye which is converted to a pigment by irreversible adsorption of the dye onto an insoluble powder. Now, lake is defined as a compound having a blend of a coloured pigment with an inert pigment. On the other hand, toners are pigments which are all-colour pigments.[2]

Nano materials are materials having a diameter of 100 nanometres (nm) or less. The nanomaterials that have similar chemistry as in mass structure might have different physio-chemical properties. Materials diminished to the nanoscale can unexpectedly show totally different properties contrasted with the properties they have on a macroscale. For instance, opaque substances may become transparent (e.g, copper); inert materials may become catalysts (e.g., platinum); stable materials turn combustible (e.g., aluminium); solids turn into fluids at room temperature (e.g., gold); or insulators become conductors (e.g., Silicon).

Nano materials are often created by top-down techniques, creating extremely small structures from larger materials, such as silicon microchips etched to provide circuits. Bottom-up methods are also possible, which involve building up structures atom by atom or molecule by molecule. One of the techniques for doing so is self-assembly, where molecules arrange themselves into structures based on their properties. The syntheses of large molecules, as well as the growth of crystals for the semiconductor industry, are examples of self-assembling compounds.

Most people refer to nanoparticles as particles less than 100nm in diameter. We define nanoparticles as particles with unique or enhanced properties due in part to their smaller size compared with larger particles of the same material. In nature, nanoparticles occur everywhere, such as products of photochemical processes and volcanic activity, as well as through the biosynthesis of algae and plants. Furthermore, they have also formed over thousands of years through combustion and food cooking - and, more recently, from vehicle exhausts. Unlike metal oxides, which are intentionally manufactured nanoparticles, synthetic nanoparticles are a minority. Compared to larger particles of the same material, nanoparticles present unique properties (such as chemical reactivity and optical properties). For example, when titanium dioxide and zinc oxide are formed at the nanoscale, they

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become transparent, yet can absorb and reflect ultraviolet light, and are used in sunscreens.

Nanoparticles are expected to find applications in cosmetics, paints, textiles and other products within the next five years; and in the long run, targeted drug delivery where they could be used to deliver drugs to specific body sites. In addition to arranging nanoparticles into layers on surfaces, nanoparticles can be arranged in layers on surfaces, resulting in a large surface area and, consequently, improved activity, relevant for a variety of potential applications including catalysts.

Since ancient times, nanomaterials have been used as pigments in different forms. To make black pigments of high opacity and stability, ancient Egyptians used the soot from oil lamps. Papyrus scrolls were excellent for writing with these as black ink. Carbon nanoparticles would be the modern term we would use for these soot particles or pigments. Soot from metallic oil lamps has long been moulded through the use of various oils and proportions, and this practice is still prevalent in many parts of India today. As a result, infants and adults alike use these soot-based eyeliners. Traditionally, these eyeliners are applied to infants in order to improve their eyesight, and supposedly to prevent diseases. A recent study showed that soot eyeliners contain a variety of metals and carbon in their nanoforms. The dark black colour is due to the nano form of carbon, while antimicrobial properties are attributed to metal nanoparticles. For centuries, nanomaterials have been used to stain glass, such as colloidal gold particles, which can be found in many Venetian windows throughout Europe.

As a pigment, nanoparticles offer a number of advantages that can be observed in many industries. Paints commonly contain titanium dioxide and silica nanoparticles. In addition to being UV filters, they can also act as antimicrobial and self-cleaning agents. In the process of integrating nanomaterials into the paint, nanomaterials are either incorporated as free powders or as stabilized particles in colloidal form. The result is that nanomaterials are firmly embedded in the paint matrix. A pigment made from nanoparticles may also produce "special effects". In jewellery and cosmetics, these are particularly useful if you want a shimmering or glittery effect. These effects are obtained using a combination of nanocrystals that are oriented in a specific way. Pigments with structural colour are obtained by systematically arranging nanoscale features in a periodic fashion. One of the newest trends in eye and nail make-up is the use of these effects, which are similar to the opalescence of butterfly wings. Cosmetic nanomaterials also have the advantage of being hydrophobic for "long-lasting" effects.

When nanoparticles are used as pigments, there are also risks associated with them, which should not be overlooked. Nanomaterials as pigments are subject to the same regulatory requirements as nanomaterials. Due to this, these pigments are safe for use, though a stigma is attached to them due to their nanotechnology. Nanoparticles are particularly small and can pass through the cellular membrane. In order to better understand the effects of these nanoparticles on humans, REACH and the regulations of the cosmetic industry have launched specific guidelines. Pigments must be tested and reported on their physical-chemical characteristics, such as size, shape, and agglomerates, during registration under REACH. The nanoparticles or their agglomerates are further tested for dustiness to ensure that they do not present a health risk to people who come into contact with nanomaterial pigments through inhalation. In addition, the REACH registration process often includes a full life cycle assessment for these pigments. The use of these substances will reduce potential health risks to humans or the environment.

1.1 Micro vs. Nano – What's and How's

Materials do exhibit different physiochemical properties when in nano state as compared to their micro or bulk state. Particles reduced to nanoscale have a higher surface area as compared to their bulk or micro particles. The change in particle size affects their properties, such as reactivity, the degree of aggregation, or bioavailability. With increased surface area, there is also an increase in the dissolution process of the compound. [10]

If we take an example of Titanium Dioxide, the pigment in bulk state is bright white and opaque. But when reduced to its nano size, it might become transparent, thereby making it useful for sunscreens. With the development of new synthetic technologies, different colored nano pigments can be obtained.

II. CLASSIFICATION OF NANOPIGMENTS

2.1 Inorganic Nanopigments

Inorganic pigments are in use since ancient times. Inorganic pigments are most effective in colouring building materials, glasses, ceramics, plastics, and glazes. Inorganic pigments are generally the Transition metal complexes. They also might be some inorganic salts.

Inorganic pigments are generally the mineral salts of various inorganic elements. They are also the transition metal complexes or even metals. Inorganic pigments are generally derived from the Earth's crust in the form of minerals.

The inorganic pigments in nanoscale have a different set of properties due to their increased surface area. These

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particles show more fineness and added hardness. Many inorganic nanopigments also show transparency which is due to the smaller particle size than the interacting wavelength of light. Coloured nanopigments may exhibit their colour properties without giving any opacity if used in higher quantities.

With the smaller particle size, the dispersibility is easier for the nanopigments, thereby ensuring the uniform distribution of the pigments throughout the material. Also, due to the higher surface area and smaller particle size, the concentration of the material required getting any physical property such as colour or UV absorbance is lesser, thereby reducing the cost of the formulations.

2.2 Organic Nanopigments

Organic pigments are generally the organic compounds (biological or synthetic) which exhibit the colour properties due to the pi bonds present in their structure.

The electron skeleton in organic compounds imparts colours to the compounds, and, as such, some important properties to the pigments. Such organic molecules have a planar conjugated chromophoric systems having functional groups such as the C=O and NH groups. In some molecules acidic and basic functional groups are present, which allows the precipitation of soluble dyes via salt and metal complex formation?

The two categories of organic pigments are –

- **Biological Pigments** - Alizarin, indigo, anthocyanins, gamboge, Tyrian purple, cochineal red, Indian yellow, rose madder, etc.
- **Synthetic pigments** - Quinacridone, Phthalocyanins, Azo dyes.

2.3 Comparison of Inorganic and Organic Nanopigments

Following table enlists the differences between inorganic and organic nanopigments:-

Table 1: Comparison of Inorganic and Organic Nanopigments

Property	Organic Pigments	Inorganic Pigments
Definition	These are the organic compounds – based on carbon chains and rings. They are coloured generally due to the pi electron skeleton present in the compound.	Inorganic pigments are generally the mineral salts and complexes of the transition metals. They may include other inorganic elements.
Chemical Composition	Carbon chains and rings	Inorganic salts – metallic salts and transition compounds, coordination complexes, minerals, and even metals
Cost	Expensive	Cheaper
Brightness	Brighter colours	Comparatively Dull colours
Colour Retention	Can easily fade due to environmental factors such as heat and light	Resistant to colour fading
Sources	Biological Origin or chemically synthesized in laboratory	Ground minerals

2.4 Hybrid Nanopigments

Hybrid means a fusion of any two different things. A common example of a hybrid can be considered as Pomato – a fusion plant made from Potato (Solanum tuberosum) and Tomato (Lycopersicon esculuntum). It has the best characteristics of both the plants, such as it can produce potato tubers as well as tomato fruits.

Similarly, the concept of hybrid nanopigments states that the fusion of inorganic and organic nanopigments to get the properties of both the pigments. So, an organic pigment is mixed with an inorganic host to create a hybrid pigment. You may choose between different types of inorganic materials based on their morphology, size distribution, and mechanical, optical, or barrier properties. There is a wide spectrum of natural or synthetic dyes that can be used as organic material. This is responsible for imparting colour, in addition to the potential for functional dyes to achieve thermochromic, electrochromic, luminescence, and other special properties.

III. APPLICATIONS

- Paints and Coatings Industry
- Ink Industry
- Medicinal and antimicrobial applications
- Cosmetic Industry
- Food and Packaging Industry
- Color TV tubes for luminescence

IV. TOXICOLOGY AND ECOLOGICAL IMPACT

- Due to the smaller particle size, nanoparticles tend to get absorbed in the body (at biomolecular level) – either by dermal or pulmonary exposure, thereby damaging the cells leading to various health issues.
- However, due to their nanoscale size, the concentration of the material can be reduced. This way, the leaching

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out and contamination of the ecosystem can be greatly reduced.

- Toxic effects needs to be researched upon, which can give a way to implement nanotechnology in pigments in a greener way.

V. CONCLUSION

As we know, pigments make our world colourful; we experience them in a completely different way with nanotechnology. Using nanotechnology in pigments - Nanopigments - is a novel approach, where we experience our world in an entirely different way.

There are a number of uses for nanopigments, including: Titania - white in bulk (white paint), but transparent in sunscreens, Thenards Blue in color TV tubes, and many more that we cannot imagine.

The ecological impact of nanopigments needs to be investigated further so the pigments can be engineered and used in a more eco-friendly manner.

VI. SCOPE FOR FUTURE PROSPECT

- Research on the methods of green synthesis of nanopigments.
- Research on the ecological impact of the nanopigments.
- Research on the toxicology of nanopigments and its reduction.

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Riya Srivastava, was born and brought up in Lucknow, India. She pursued her Bachelors of Science from University of Lucknow with Botany and Chemistry as main subjects. She went ahead with Chemistry as the main subject and pursued Masters of Science in Chemistry from Kalinga University, Raipur. She likes researching and literature surveys.

Dr. Manisha Agrawal, professor, and dean of the Chemistry department from Rungta College of Engineering and Technology has come up with a solution via agro-waste that will utilize dry wood, fruits, and coconut scrub to solve the problem of “foam creation” in drainage systems and streams. She told, “State government has appreciated the project and the best part of using agro-waste is that the cost of purification will be reduced by 30%” Dr. Agrawal has also come up with the concept of bio-filter charcoal to eliminate the process of froth production in water bodies.

Mrs. Sarvaree Bano, Assistant professor of the Chemistry department from Kalinga University, Naya Raipur, C.G. She pursued her Bachelors of Science from Guru Ghasidas University, Bilaspur with Botany, Zoology and Chemistry as main subjects, .M.Sc. (Chemistry from Guru Ghaidas university (Bilaspur) and she holds a M.Phil. (Chemistry) degree from Dr. C. V. Raman University. She is Pursuing Ph.D. from CSVTU Bhilai.

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APPENDIX

Table 2: Important Inorganic Nanopigments

Pigment Category	Pigment Name	IUPAC Name	Formula	Colour	Applications
Titanium-based pigments	Titania	Titanium(IV) oxide	TiO_2	White; Transparent in Nanoscale	Paints, Surface Coatings, Plastics, and Paper. Also in Sunscreens due to its higher Sun Protection factor (SPF) and transparent appearance
Cobalt Based Pigments	Cobalt Blue or Thenards Blue	Cobalt(II) oxide-aluminium oxide; Cobalt(II) aluminate	$CoAl_2O_4$	Blue	Color TV tubes as contrast-enhancing luminescent pigments, high-end optical filters, magnetic recording media, and as a heat-resistant ceramic
Zeolites	Aluminosilicates		$Na2Al_2Si_2O_8$	Green (Natural Grade)	Catalysis, separation and ion exchange processes, nanosized zeolites assembled in films and three-dimensional constructs are used as optical devices, separation membranes and reactors for immobilization of chemical sensitive compounds
Zinc Based Pigments	Zinc White	Zinc Oxide	ZnO	White	Sunscreens; Antibacterial properties; Can be used in food packaging
Carbon Based Pigments	Carbon Black	Carbon	C	Black	Conductive pigment - electronics, plastics, coatings, inks, and green technology; reinforcing filler and in the rubber industry
Gold and Silver Nanoparticles	Metallic Silver	Silver	Ag	Silver	Nano biotechnology, biosensor studies, study of cell structures and targeted drug delivery. The bactericidal properties of silver are associated with the nanoparticles' slow oxidation and slow release of its ions.
	Metallic Gold	Gold	Au	Gold	
Iron Oxide based Pigments	Red Oxide	Iron(III) oxide or Ferric oxide	Fe_2O_3	Dull Red	Food colourings, Paints and coatings, concrete or metallic substrates
	Yellow Ochre	Iron(III) oxide-hydroxide; Ferric oxyhydroxide	$FeO(OH)\cdot H_2O$	Yellow	

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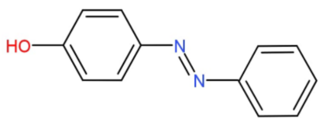
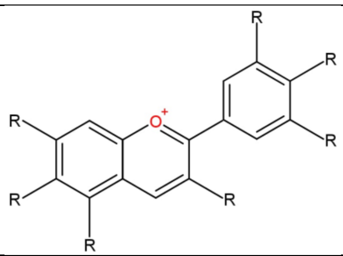
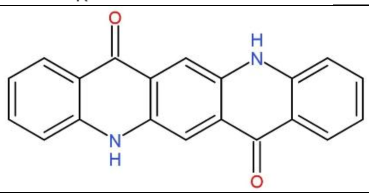
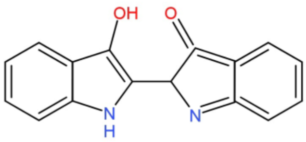
Table 3: Important Organic Nanopigments

Pigment Category and Name	IUPAC Name	Molecular Structure	Colour	Applications
Azo Dyes - Pigment Yellow 12	Derivatives of diazene (diimide), HN=NH, wherein both hydrogens are substituted by hydrocarbyl groups		Yellow to orange	Used in coatings and paints, food colorants, textiles, leather industries, plastics and rubbers
Anthocyanins	Cyanidin-3-glucoside - Most common		Red to purple to blue	Natural food colorant and dyes, Pharmaceutical use due to antioxidant properties
Quinacridone – Pigment Violet 19	5,12-Dihydroquinolino[2,3-b]acridine-7,14-dione		Magenta to Violet	Paints and Coatings, outdoor paints, printer ink, tattoo inks, watercolour paints, and colour laser printer toner
Indigo – Indigo Blue	2-(3-hydroxy−1H-indol-2-yl)indol-3-one		Blue	Medical, cosmetic, and food industries, manufacture of functional fibers, polymers, semiconductors, and sensors

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