Infrared Reflective Inorganic Pigments

Ashwini K. Bendiganavale and Vinod C. Malshe*

(Retd) Prof. Paints Technology, University Institute of Chemical Technology, Matunga, Mumbai, 400019, India

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Abstract: Solar energy is essential for human race. It spreads itself thin on the entire surface of the globe. The large buildings, which are now essential for the world's growing population, need to be made comfortable for its residents. In certain parts of the year these radiations are not required for the comfort of the residents. If the buildings are allowed to receive these radiations, the expenditure of cooling is excessive. Coatings that reflect the infrared radiation in the near IR region responsible for heat from the solar radiation are formulated with special pigments. In the present paper, patents devoted to preparation of these pigments have been reviewed. Some research work carried out at University Institute of Chemical Technology has also been included. It has been found that there are no theories to predict the infrared reflectivity of a pigment and the best way to find one is to scan the available pigments for their IR reflectivity.

Keywords: Infra red reflection, inorganic pigments, cool roof coatings, high performance pigments.

INTRODUCTION

Pigments are inorganic or organic substances that are insoluble or substantially insoluble in water or the organic medium in which they are used as dispersions. They impart color, opacity, mechanical rigidity and reinforcement to the continuous phase in which they are dispersed. Paint is a fine dispersion of pigments in binder(s) in the presence of solvent (s) and a small amount of additives. The final properties of the paint or coating depend on the properties of the binder, pigments or also on the additives. Pigments alter the appearance of the coating by selective absorption or by scattering of light. Pigments are classified on the basis of their performance as decorative pigments and protective pigments. Pigments also impart certain special properties to the coatings such as reflection of infrared radiation [1]. Light or electromagnetic radiation falling on any object meets three fates. It can be reflected, absorbed or transmitted. Any or all three can occur totally or selectively on the entire spectrum of electro magnetic radiation. (This means a substance can reflect in visible region, absorb in UV region and transmit in Infra Red region or any other combination of the three.) The development of infra red reflection phenomenon seems to have stemmed from the observation that radar frequency reflective pigments have been developed and used in the defense for making airplanes invisible to radar. For a common man, it is very difficult to comprehend this phenomenon since human beings cannot see radar waves. It is true for IR reflecting pigments also.

Light energy from the sun spans a wide range of wavelengths. Much of the total energy is absorbed in our atmosphere and never reaches the Earth's surface [2, 3].

The light that reaches the Earth's surface ranges from 295-2500 nanometers (nm) in wavelength. The human eye is sensitive to only a part of the electromagnetic spectrum. Apart from the visible region, pigments also interact with other wavelengths of light in the electromagnetic spectrum. These interactions can produce interesting effects on the coating properties.

The sun's energy that reaches the earth's surface is divided in to three main parts:

Ultraviolet Region (295-400 nm):

The ultraviolet region starts at 295 nm. At this point the atmospheric cut-off occurs. This light is full of energy most suited to break several bonds, which hold the polymers, and is also responsible for sunburns. UV accounts for about 5% of the sun's energy that reaches the earth's surface. It is responsible for degradation of binder of the coatings because the energy level is enough to break down the primary bonds.

Visible Region (400-700 nm):

Around 50% of the sun's energy occurs in the visible region of the electromagnetic spectrum.

Pigments selectively absorb the visible light and reflect the remaining. If an object reflects the entire visible wavelength range, then it is white. If some regions of this light are absorbed and others reflected, then the object is colored e.g. a blue pigment absorbs all wavelengths except blue. It appears blue because it reflects only blue light absorbing all others in the visible region. A black surface appears black because it absorbs everything in the visible region and reflects nothing in the visible region. Thus, the visible region consists of wavelengths that give us the perception of color.

Infrared Region (700-2500 nm):

Forty-five percent of the total solar energy is in the non-visible infrared region. Heat is a direct consequence of infrared radiation incident on an object. Infrared radiations range from 700 - 2500 nm wavelength. The heat-producing region of the infrared radiations ranges from 700 - 1100 nm. These radiations on absorption result in heating up of the surface.

Infrared reflective inorganic pigments are complex inorganic color pigments, which reflect the wavelengths in infrared region in addition to reflecting some visible light selectively. The reflectivity and absorptivity of the pigment

*Address correspondence to this author at the 33-34, Building No.10, Kamdhenu, Kalpataru Projects. Hari Om Nagar Mulund (E) Mumbai 400081, India; Tel: 00912225320153; Fax: 00912225821588;
E-mail: vcmalshe@gmail.com

1874-4788/08 $100.00+.00

are independent of each other. Thus an IR reflective pigment may have any color. These pigments are synthesized by subjecting mixtures of metal hydroxides, nitrates, acetates or even oxides, to very high temperatures in a process called calcination. Metal oxides or salts are blended together and strongly heated, generally at temperatures of over 1000°C. At the calcining temperature the solids themselves become reactive. Metal and oxygen ions in the solids rearrange to form new, more stable crystal structures such as spinel or rutile structures [4].

IR reflective pigments are increasingly used for roof and building coatings because of their excellent weatherability. They have an ability to maximize reflectivity in the near infrared region. These IR-reflective pigments find increased use as the formulators make an attempt to produce dark coatings and minimize heat buildup in the underlying structure. Nickel manganese ferrite blacks (Pigment Black 30) and iron chromite brown-blacks (CI Pigment Green 17, CI Pigment Browns 29 and 35) are some of the infrared reflective pigments that are used to provide dark colors with reduced heat buildup. Other commercially available infrared reflective pigments are Pigment Blue 28 Pigment Blue 36, Pigment Green 26, Pigment Green 50, Pigment Brown 33, Pigment Brown 24, Pigment Black 12 and Pigment Yellow 53 [5].

In urban areas, the design of roofs has a major influence on the heat absorption of sunlight. The hot buildings also known as “Concrete Jungle” radiate heat and warm the air in the surrounding. If there are several such buildings in the vicinity, the combined effect leads to a phenomenon known as ‘Urban Heat Island Effect’. The amount of heat radiated in the surroundings varies depending on the roof construction, type, elevation and also the color of the coating used. Significant amount of heat is also absorbed into the building by means of conduction. With such increasing heat energy in the building, there is a need for variable energy in the form of air-conditioning to keep the interiors of the building cool and tolerable for people to work and live in them. To reduce the increasing demand for energy consumption for air conditioning, there is a need for cooler roofs. Reflecting most of the sun’s heating energy minimizes the amount of energy absorbed by the building.

These pigments are highly stable and chemically inert. They can withstand the chemically aggressive environments and still retain their color. They do not fade in the presence of ozone, acid rain, SO_x, NO_x or other air pollutants common in industrial areas. They even remain colorfast in the presence of strong acids, bases, oxidizing or reducing agents. They are non-migratory, and do not dissolve or bleed when in contact with solvents. Because of these properties, these pigments last as long as 30 years in outdoors. Formulating paints with them is a major challenge since the binders degrade much faster. The most expensive component of the formulation is the IR reflective pigment.

In addition to excellent chemical stability, these pigments are also stable to high temperatures. Due to high heat stability, they can be used for high-heat coatings, such as muffler and stove coatings, fireplace paint, and high-heat powder coatings. Porcelain enamel and decorative ceramic coatings also use these pigments.

REFLECTION MECHANISM OF INFRARED RADIATIONS

The infrared reflective pigments have the following properties [6].

They do not absorb in near infrared region. They either reflect it or transmit it.

Their refractive index is different from that of the binder in the infrared region. This causes diffused reflection in IR region. If the refractive index of the pigments in the IR region is similar to that of the binder’s refractive index in the IR region, the pigment would be transparent to near infrared light (NIR). In such a case, any reflection in the near infrared region would be due to the undercoat.

Absorption of light occurs when light energy promotes electrons from one bonding state to another. If light of a different wavelength is used to cause this energy transition, it will not be absorbed e.g. iron chrome blacks absorb light through the visible region. This means there are electronic transitions responsible for absorbing light with wavelengths of energy from 400 - 700 nm. Light of lower energy (>700 nm) is not absorbed. In this case, a beam of light with a wavelength of 1500 nm is too low in energy to cause any electronic transitions in the material. Thus it will not be absorbed. Instead the 1500 nm light beam is refracted, reflected and scattered (depending on the refractive index) leading to diffuse reflection of NIR light. There is no method to predict the IR reflectivity of an inorganic or organic compound. This property appears to be an inherent characteristic property just like density, thermal conductivity, color, refractive index etc.

BENEFITS OF INFRARED REFLECTIVE COATINGS

General benefits:

- Longer life-cycle due to less polymer degradation and thermal expansion due to lower temperature.
- Aesthetically pleasing colors.
- Cooler to touch for better handling
- Improved system durability and less thermal degradation.

In addition to the above mentioned benefits, the IR reflective coatings also have certain Roofing benefits:

- Less heat to transfer into buildings.
- Reduced ‘Urban heat island effect’.
- Low energy demand for air conditioning, particularly in equatorial regions.
- Reduction in air pollution due to low energy usage, power plant emissions, and reduction in urban air temperatures.
- Installation crews can work longer during the day before the roof gets too hot to work on.
- Very high durability coatings. Some coatings have been in use for as long as 25 years.

FACTORS AFFECTING INFRARED REFLECTIVITY

Some factors that can affect the coating's infrared reflectivity are individual pigment selection, milling and dispersion, particle size, mixing infrared reflective pigments, opacity and contamination.

- Individual pigment selection: Pigments having highest reflectivity in the near infrared region must be selected for making infrared reflective coatings. Pigments should be selected on the basis of required shade depending on the L, a and b value of the pigment.
- Dispersion: These pigments are compatible with all types of solvent and water-based coating systems such as acrylics, polyesters and fluoropolymer systems. For complete dispersion and optimum properties, pigments should be dispersed in a small media mill to obtain the required fineness of grind. The pigments should not be over ground, as additional grinding will break the particles, affecting the color and also the infrared reflectivity of the pigments.
- Blending pigments: Care must be taken while formulating a coating with more than one pigment. A combination of two infrared reflective pigments can increase the total reflection of the coating. But in some cases where different pigments absorb in different regions, the total reflectance becomes less than the reflectance of the individual pigments. In such a case, the absorption overpowers scattering. Thus, care must be taken while selecting a combination of pigments to make infrared reflective coatings.
- Opacity: The infrared reflective pigments have high visible opacity. These pigments only scatter or transmit the infrared radiations. Thin films may not scatter and reflect all the infrared radiations from the coating and may allow the radiations to pass through to the substrate. Thus, such coatings have visual opacity but are not completely opaque to infrared light. Thus higher coating thickness may be required for the coating to be opaque to infrared. Apart from film thickness, pigment volume concentration also plays an important role in deciding the opacity of a coating to infrared radiations.
- Contamination: Contamination occurs when two infrared reflecting pigments absorbing at different regions are mixed together. It is worsened when an infrared reflective pigment is mixed with an infrared absorbing pigment. Such contaminations drastically affect the total solar reflectance on the coatings [3].
- Particle Size: Particle size of the pigment is a very important parameter. For highest reflectivity, the particle size should be more than half the wave length of the light to be reflected. Thus for reflecting infra red light of 700-1100 nanometers wave length, particle size should be at least 0.35 to 0.55 microns [1]. Excessive grinding and dispersion may therefore be counter productive.

Various attempts have been made to synthesize IR reflective pigments and coatings. The synthesis strategies can be roughly divided in three parts.

1. Coating a thin film of glass or mica with an infra red reflecting substance and holding it there by physical forces.
2. Coating a thin film of glass or mica with a metallic surface. Metals are known to reflect almost entire visible and near IR radiations. (For visible region, the well known exceptions are gold and copper which are respectively yellow and red)
3. Synthesize inorganic crystalline substances, which have good pigmentary properties and find out if these are also IR reflective

Few attempts are listed as follows:

Infrared reflective metallic pigments are manufactured by The Shepherd Color Co. using Micro Mirror Technology. These pigments have high brilliance and sparkle and also good infrared reflectivity. Borosilicate glass, having high strength and excellent chemical resistance, is used as the substrate in these pigments. A sub-micron layer of metallic silver is deposited on the glass surface. The uniformity of the silver coating is important to cover the glass surface completely and also to minimize the surface roughness that would diffuse the incident radiation. These pigments are resistant to stress and shear. There is no need to soak them for pre-dispersion. They can be incorporated in coatings using low shear mixing equipments. They are capable of surviving a degree of vigorous mixing without changing the appearance or brilliant effect. These pigments are produced in two different crystal shapes - lamellar and spherical. The lamellar grades are based on glass plate substrate having thickness of 5 microns. They have a very narrow particle size distribution for maximum contrast. There are two types of spherical grades. One of them has a solid glass substrate and the other one has silver coated hollow microspheres. The orientation of these particles results in excellent reflection. Most of the applications of these pigments are based on their aesthetic properties. They are used in coatings for canned beverages, packaging of consumer goods, candles, decorative ornaments, musical instruments and fishing lures. The effect of these pigments is prominent in sunlight. They produce dazzling effects on custom automobiles, motorbikes, bicycles, boats, skis, spas and swimming pools. These pigments also find applications in cosmetics, apparels, sunglasses and cell phones. Thus, silver coated glass flake pigments are used to achieve brilliant effects without limitations of conventional metallic pigments. They can be incorporated in any coat of the paint system, in combination with transparent or opaque colorants [7].

US Patent 20060159922A1 describes synthesis of infrared reflective pigments, in form of flakes, for use in paints, composite gelcoats, varnishes and other coating formulations [8]. The flakes comprise an infrared reflective core having thickness of less than 0.2μm and an infrared transparent material coated on the surface of the core. The transparent layer comprises a binder with optionally a colored material. The transparent layer provides color and mechanical strength along with chemical resistance to the core material. The core comprises metallic or conductive oxide material. Different combination of colorants can be used on either side of the core surface to provide different shades.

In another invention, Anthony David Skelhorn *et al.* [9] have developed a coating system with high infrared reflectivity and low thermal conductivity. These coatings comprise water-based, solvent based, single component or multi component, cement or gypsum based binder systems. The coatings also comprise infrared reflective extenders, pigments and hollow micro-spheres made up of glass, ceramic or organic polymers. Extenders like calcium carbonate, crystalline and amorphous silica, silicate minerals such as Talc, kaolin, calcined clay, wollastonite, nepheline syenite, feldspar, mica, attapulgite clay, bentonite and organically modified bentonite, alumina trihydrate, aluminum oxides, barytes and lithopone are known to have considerable infrared reflectivity. Hollow micro-spheres like glass micro-spheres of different glass compositions, having different diameter to wall thickness values and different particle diameters, Ceramic micro-spheres such as 3M's Z-light Spheres, Cenospheres, fly ash; or micro-spheres based on organic polymer composites like polymers or copolymers of acrylic materials in form of dry powder or dispersions such as Rhopaque by Rohm and Haas, or copolymers of vinylidene chloride and acrylonitrile such as Expancel by Expancel, Inc. were used in the composition. Commercially available infrared reflective pigments were also used in the coating composition. The hollow micro-spheres reduced the thermal conductivity of the coatings, whereas the IR reflective pigments and extenders increased the infrared reflectivity of the coatings. The thermal primers and coatings prepared by using the above mentioned raw materials were found to have excellent infrared reflectivity and low thermal conductivity.

U.S. patent 6454848 describes development of solid solutions having corundum-hematite crystalline structure which are useful in inorganic pigments [10]. The solid solutions contain a host component having a corundum-hematite structure and a guest component of one or more elements such as aluminum, antimony, bismuth, boron, chrome, cobalt, gallium, indium, iron, lanthanum, lithium, magnesium, manganese, molybdenum, neodymium, nickel, niobium, silicon, tin, titanium, vanadium, and zinc. Thoroughly mixing the compounds, containing the host and the guest components and calcining at high temperatures to form solid solutions having corundum-hematite crystalline structure formed the solid solutions. These compounds exhibit dark colors and excellent reflectivity in the near-infrared region.

Another invention describes preparation of IR reflective pigments by coating a white pigment with IR reflecting colorants [11]. Yanagimoto Hiromitsu *et al.* used colorants like azo, anthraquinone, phthalocyanine, perinone/perylene, indigo/thioindigo, dioxazine, quinacridone, isoindolinone, isoindoline, diketopyrrolopyrrole, azomethine, and azomethine-azo for coating on the white pigments. White pigments like titanium dioxide or zinc white and extenders like calcium carbonate, barium sulfate, alumina, silica, clay, activated clay, aluminum powder, stainless steel powder, and organic plastic pigments were used in different combinations as the white pigment base. The colorants and white pigment base were used in the form of dispersions. The dispersants used were high molecular weight components obtained by copolymerizing hydrophilic monomers such as acrylic acid, methacrylic acid, dimethylaminoethyl methacrylate with styrene or methacrylate ester, having hydrophilic end groups. The IR reflective colorant dispersions and white pigment dispersions were mixed in a conventional mixer such as dissolver, where the white pigment was coated with the IR reflective colorant. The IR reflective pigment was obtained by drying the resulting mixture. Even though the coloring component is organic, the temptation of thinking of these as IR reflecting organic pigments must be completely avoided. The IR reflective component is the inorganic part.

Several existing inorganic pigments in the range of manufacturers servicing the ceramic industry were found to have IR reflecting character. These have found additional applications in the cool roof coatings. Figure **1** shows a range of different commercially available infrared reflective pigment shades.

APPLICATIONS OF INFRARED REFLECTIVE PIGMENTS

Building products

Exterior building products are designed such that the heat build-up can lead to part failure and increased energy costs. IR-reflecting pigments are used for different building applications.

<u>Coatings:</u> Infrared reflective pigments are widely used in roof coatings. They are suitable for all types of architectural finishes; including highly-alkaline masonry coatings (e.g. silicate paints).

Apart from roof coatings, window coatings have also been synthesized. These coatings transmit the visible light and reflect the infrared light from the sun’s radiations. Modern architectural designs employ the use of large glass areas. These contribute to the aesthetic appearance of the building and reduced maintenance, but also increase the energy consumption. Large glass surfaces in buildings account for large heat losses during the winter season and excessive heating by direct solar radiation in summer. The latter effect is a major contribution to energy cost since it costs three to six times more to cool a building than to heat it [12].

The infrared reflective properties of thin metallic films of metals such as gold can be utilized for making window coatings. These films, when sufficiently thin, transmit visible light and reflect the infrared portion of the incoming sunlight. Heat reflective gold coatings on architectural glazing have two main disadvantages. The thin gold films, even when transmitting visible light, are highly reflective not only to infrared radiation, but also to visible sunlight. This property results in a metallic glare, which is objectionable to the observers. In addition, gold is expensive even though it is used as only a thin film. The cost disadvantage of a gold coating can be overcome by replacing it with non-noble metal films. However, such films still exhibit metallic glare and also have stability problems due to corrosion, thus requiring the deposition of additional layers for protection against oxidation. Considering these factors, Haacke

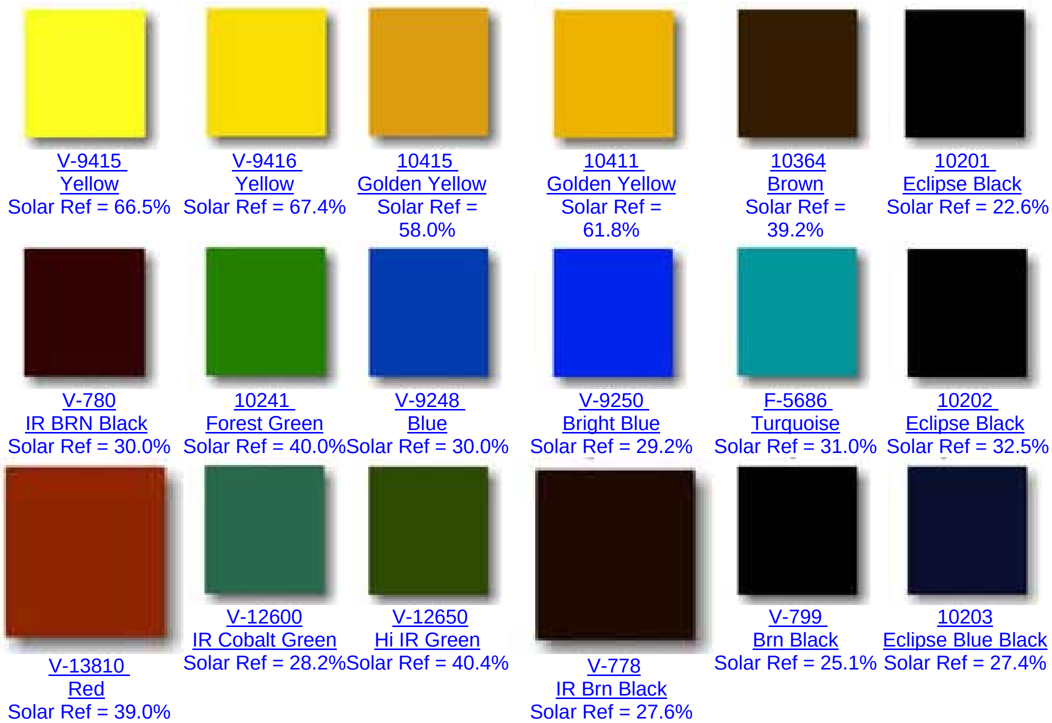

Fig. (1). Commercially available IR reflective pigment shades

Gottfried has used certain semiconductor metal layers as an alternative to heat reflective metallic films [13]. He has stated that if the energy gap of these materials is large (approximately 3 eV), they are transparent to visible light. Also, if the free electron concentration in these semiconductors exceed to a large extent, these films also give high infrared reflectivity.

Cadmium stannate (Cd_2 SnO_4) is one of the most transparent, heat reflecting semiconductors, which Haacke Gottfried has used for making infrared reflective coatings. CdO, SnO_2 and CuCl are mixed thoroughly to make a homogenous mixture and heated in an alumina crucible for six hours at 1050°C. The cadmium stannate crystals have shown orthorhombic structure. Cadmium stannate films on a silica plate reflect infrared light at approximately 1.5 micron thickness. These films give 80% reflectance at 2 microns film thickness and 90% reflectance at 6 microns thickness. These properties make cadmium stannate films highly suitable for greenhouse window applications. It has also been found that doping of cadmium stannate with copper increases the infrared reflectivity and films made out of this material can also be utilized for architectural window coatings.

Vinyl window and siding: Rigid PVC is a temperature sensitive product and it distorts, as it gets hotter. Vinyl siding and window and door profiles tend to wrap and twist out of shape if not correctly manufactured. Regular pigments used to achieve color often make the warping tendency much worse. Infrared reflective pigments can be used in such cases. They enable colors other than white to be made and also reduce the warping and twisting.

Cement, concrete and pavers: Infrared reflective pigments do not fade and counter heat build-up when used in cements. Infrared reflectance allows the color to stay true for a longer period of time. Cement pavements remain cooler during hot climates.

Automotive application: Dark colored cars get hotter during summer. Dark seats may be easier to maintain, but they can get uncomfortably warm. Hot instrument panels, consoles and dashboards become brittle with age, and exude plasticizer and other organic compounds. Moreover, increasing the cooling load of the air conditioning unit to reduce heat discomfort may lead to certain other problems. Automobile engines are being downsized to reduce the weight and improve fuel economy. They are less able to handle the power drain of the larger air conditioners. Air conditioners are a major source of chlorofluorocarbons (CFC) released into the atmosphere. Increased cooling load leads to larger air conditioning units, which increases this problem. Thus, there is a need for new technologies to reduce the solar heat loads and to allow reduction of air conditioner size. These cooling alternatives would result in reduced CFC emission and increased vehicle fuel efficiency. Thus there is a possibility of over all reduction of carbon dioxide emanating from fossil fuels and making road transport more economic.

Infrared reflective pigments can be used in the coating formulation to reduce the heat build-up of the car. These pigments give best performance with respect to color-fastness, IR-reflection and other properties for several years.

The above-mentioned coatings only reduce the infrared reflection of the coatings from the metal surface. The automobile glazing still contributes to the heat problem by allowing infrared radiations to pass through. US Patent 5405680 describes the use of a coating comprising a semimetal and a selectively emissive metal [14]. The semi-metal film reflects the incident solar radiation and transmits visible light. The selective emissive material provides a means for radiating the infrared radiation, thereby cooling the enclosure interior via radiation. There are several known semimetals that reflect in the range of 650-800 nm. Some of them are rare earth and other metal borides and chalcogenides, such as LaB_6, LaTe, and SbS_3. It has been seen that the semimetal film made by using LaB_6 exhibits strong reflection through the entire infrared region. The selective emissive materials used are metal oxides, particularly heavy metal oxides, such as zirconium oxide and thorium oxide. In some cases, aluminum oxide has also been used. These have been studied by applying separately on the glass surface as thin films, combining together and applying as a single thin film, converting them into a paint wherein they are retained as suspended particles and embedding them into the glass structure itself. In all the four cases, these materials have shown good infrared reflectivity.

Apart from automobiles, these coatings can also be used in domestic household applications.

<u>Military application:</u> Chlorophyll is the pigment that makes plants green. To camouflage military equipment and personnel, synthetic green pigments are incorporated into the coatings. However, conventional green pigments do not resemble chlorophyll in the infrared region. They absorb infrared light, whereas chlorophyll reflects it [10]. (Chlorophyll thus appears to be the only known Organic IR reflecting pigment and this also explains why the shade of trees is cooler than the surroundings in hot summer). As a result, an improperly formulated camouflage color appears black against a bright background when viewed through IR-imaging equipment. The use of infrared reflecting pigments makes possible the formulation of materials that look like foliage to the human eye, and also to the infrared camera. These pigments also reflect solar energy from the decks of ships. Thus, solar-induced heat build-up is minimized, and so is the energy consumption to cool the vessel's interior.

US Patent US6468647 describes the use of colored metallic pigments such as aluminum and mica flakes for good infrared reflectivity [15]. According to the patent, color has been incorporated on the metallic surfaces in such a way that it does not interfere with the ability of metallic pigments to control infrared reflectivity. Many commercially available pigments have been burnished into the metallic surface to yield a modified surface, which retains the color of the pigment, and gives very high infrared reflectivity. This burnished surface technique holds the pigment particles so strongly that the pigment cannot be removed by normal washing or by solvents. The amount of pigment burnished into the surface may be varied to achieve various shades of color. Pigments with good hardness and dispersed particle size of less than 1 micron have been used for the burnishing process. The burnishing process can be carried out in different ways. The metal particles and the pigment particles can be subjected to thorough mixing in a vibratory tumbler. They can also be subjected to ball-milling for several hours to get a proper coating on the metal surface. By this process, the pigment particles are mechanically bound to the surface of the metal and are not easily removable by washing or handling. The pigment particles remain on the metallic surface when the colored particles are utilized in coating formulations. These coatings can be applied to metal, plastic, composite, or fabric substrates to yield products, which have the desired infrared reflectivity and the desired visual color. These materials can find wide applications in military applications.

<u>Infrared reflection from fire:</u> Fire-resistant paints have been formulated for two main reasons. One is to reflect heat and the other is to insulate from heat. These coatings thus keep the temperature of the coated combustible substrate below the ignition temperature.

There are two types of fire retardant coatings:

1. Coatings that do not burn when exposed to fire, generally referred to as "fire resistant"
2. Coatings that insulate the flammable substrate, keeping its temperature lower than the combustion point, generally referred to as "intumescent".

In addition to these coatings, some pigments chemically inhibit fire. E.g. antimony trioxide when combined with halogenated organic compounds, gives the product, antimony oxy halide, which smothers the fire by excluding oxygen. An important quality for the effectiveness of fire retardancy is the ability of the coating to reflect heat. The radiation of heat from a fire to an unaffected area of the structure is a decisive factor in the spread of the fire [16]. Use of white or pastel paints has been made in most of the cases for heat reflection. A combustible structure is coated with a white or pastel paint to reflect infrared radiations and delay the spread of fire. Titanium dioxide is a common white pigment that is being used for this application as it has good infrared reflectivity.

The US Patent US5811180 describes the use of certain infrared reflective pigments to the coating composition to enable the reflection of the fire radiation [17]. These pigments have particle size between 1-2 microns. The infrared reflective pigments include metallic flakes such as aluminum flakes, and mica flakes coated with a material of high refractive index. The infrared reflective property of the metal or coated-mica flakes is not dependent on pigment size. Some materials having high refractive index described in the patent for coating on mica are Fe_2O_3 - a red pigment, anatase and rutile TiO_2, Cr_2O_3 - a green pigment, ZnS, Sb_2O_3, ZrO_2, and ZnO. Thicker coatings than that are needed for colored coatings increase the infrared reflectivity of the pigments. Coated synthetic fluorophlogopite micas in which IR absorbing OH groups have been largely eliminated by the use of fluorine substitution also act as an infrared reflective pigment substrate. To achieve high reflectance over a wide spectral range, more than one type of coated mica can be used.

Another type of infrared reflective pigment for use in coatings, which is not IR transparent, is aluminum metal in the form of thin flakes. Aluminum is highly reflective in the

IR due to the high concentration of mobile electrons. "Leafing" aluminum paints are particularly more reflective. These coatings contain overlapping pigment flakes, which are parallel to and concentrated near the surface of the binder.

Coatings are made from these materials and used for coating the surfaces of combustible materials such as wood, polymers, fabrics, paper, etc. These coatings reduce the fire hazards associated with these materials. These coatings can prevent substrate ignition despite the proximity of a heat source and, if ignition occurs, can cause a decrease in the rate of fire spread. These coatings are not limited only for the substrates that are directly combustible. Flammable liquids are often stored in non-combustible, painted, metal containers. These containers can be coated with such an infrared reflective coating to keep the container surface cooler, and thus its flammable liquid contents cooler, when a fire is nearby.

EXPERIMENTATION

We undertook a very ambitious research program for synthesis and evaluation of infra red reflecting pigments. Little did we know that theories were simply not available to predict physical properties such as IR reflectivity. A series of discussions involving some of our colleagues from physics and dyes departments met with a dead end. Thinking that Titanium was an important ingredient of infra red reflecting materials, we tried some synthetic procedures for preparation of titanium bearing pigments including elements from transition group known to impart colour. Several pigments were synthesized using Cobalt, Iron, Nickel and Manganese in different atomic proportions and evaluated for their IR reflectivity. None of the products so synthesized displayed any significant IR reflectivity, though most displayed exceptional pigmentary properties and a range of colours.

The parameters responsible for IR reflectivity of a pigment seem to be unknown. Just like other physical properties of matter such as density, transparency or opacity, refractive index, color, thermal conductivity, electrical conduction or resistance, there seems to be no method to predict if a substance would be able to reflect infrared radiations or not. We were reminded of the extensive research work carried out all over the world in thousands of laboratories for inventing super conductors and semi conductors, which were inorganic materials. Our search to correlate structural parameters to any of the physical properties using available theories of physics (known to us) met with a dead end. Why an element or a compound behaves in a particular way appears to be as yet unpredictable. An IR reflecting pigment may contain a given number of elements in a specific proportion. Altering the proportion or the temperature of calcination results in completely different product. In order to correlate the IR reflectivity of a pigment with different parameters, the only available method was to screen and search. This was adopted to look for any unreported infrared reflective compounds. As our studies have indicated, this approach appears to have the biggest potential to find new products.

Ceramic pigments are inorganic compounds with high pigmentary properties. Several commercial ceramic pigments were screened by a simple laboratory test. Certain commercially available ceramic pigments were used for the test as they cover the entire transition elements series (except noble metals) based on the information provided by the suppliers. These have good pigmentary properties and are also manufactured by calcination at high temperatures as that of the commercially available infrared reflective pigments. These pigments were obtained from Ceramitec Industries, Thane (Maharashtra, India). Some commercially available infrared reflective pigments were also received from Shepherd Color Company, USA, for the test.

Experimental

1.Chemical Analysis

No efforts were made to chemically analyze the pigments.

2.Preparation of Paints

The pigments were used as received and only dispersed (not ground) for preparation of the paints. The pigments were converted into coatings using Styrene-acrylic emulsion with 50% solids as the binder with pigment to binder ratio of 1: 1.

3. Evaluation of performance

The samples were evaluated using the Lab test devised by us to evaluate the pigment samples used in the present study. The coatings were applied on cement roof sheet panels with 6 mm thickness. The panels were exposed to Philips 250 W, 220-230 V Infrared lamp. The distance between the panel and the lamp was maintained at 30 cm. A thermocouple at the other side of the panel recorded the temperature. The panels were allowed to equilibrate for an hour before the temperature was recorded. The same procedure was followed for an uncoated panel. The difference in the temperatures at the reverse side of both the panels showed whether the pigments used were infrared reflective or not. Figure **2** shows the experimental setup for measuring the infrared reflectivity of pigments and Table **1** shows a list of all the pigments and coatings tested for IR reflectivity.

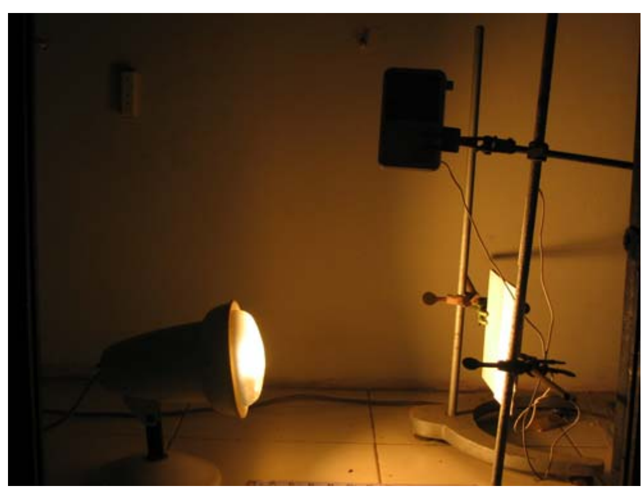

Fig. (2). Experimental setup for measuring the infrared reflectivity of pigments.

Table 1. List of Different Pigments Characterized for IR Reflection

Sample	Manufacturer	Temperature of Uncoated Panel (°C)	Temperature of Coated Panel (°C)	Temperature Difference (°C)
Synthetic Rutile (Emulsion Paint)	CMRL	60	49	11
Synthetic Rutile (Synthetic Enamel) 18% PVC Cement roof Panel	CMRL	60	50	10
Synthetic Rutile (Synthetic Enamel) 18% PVC MS Panel	CMRL	60	58	02
TiO_2 Rutile Enamel 18% PVC Cement roof Panel	Local Manufacturer	60	49	11
TiO_2 (Anatase) Synthetic Enamel 18% PVC Cement roof Panel	Local Manufacturer	60	50	10
TiO_2 Rutile Enamel 18% PVC MS Panel	Local Manufacturer	60	57	03
TiO_2 (Anatase) Synthetic Enamel 18% PVC MS Panel	Local Manufacturer	60	57	03
PY195 Cement roof Panel	Shepherd Color	60	55	05
PY 253 Cement roof Panel	Shepherd Color	60	51	09
PBR 352 Cement roof Panel	Shepherd Color	60	56	04
FL 105 Cement roof Panel	Shepherd Color	60	47	13
PY 182 Cement roof Panel	Shepherd Color	60	44	16
PY 195 Cement roof Panel	Shepherd Color	60	46	14
Brown 12 Cement roof Panel	Shepherd Color	77	57	20
Blue 385 Cement roof Panel	Shepherd Color	77	60	17

(Table 1) Contd…

Sample	Manufacturer	Temperature of Uncoated Panel (°C)	Temperature of Coated Panel (°C)	Temperature Difference (°C)
Blue 217 (VI) Cement roof Panel	Shepherd Color	77	60	17
Green 179 Cement roof Panel	Shepherd Color	77	62	15
Black 411 Cement roof Panel	Shepherd Color	77	59	18
Green Cement roof Panel	Shepherd Color	77	64	13
White Insulating Coating Cement roof Panel	Local Manufacturer	60	52	08
Co, Al, Zn Ceramic Pigment Cement roof Panel	Ceramitec Industries	60	53	07
Co, Al, Fe, Zn, Sn Ceramic pigment Cement roof Panel	Ceramitec Industries	60	55	05
Co, Al, Si, Zn Ceramic Pigment Cement roof Panel	Ceramitec Industries	60	61	- 01
Co, Cr, Fe, Al, Zn Ceramic Pigment Cement roof Panel	Ceramitec Industries	60	55	05
Fe, Cr, Mn, Co, Ni, Ceramic pigment Cement roof Panel	Ceramitec Industries	60	61	- 01
1342 Brown Cement roof Panel	Ceramitec Industries	60	57	03
1432 Brown Cement roof Panel	Ceramitec Industries	60	57	03
2133 Brown Cement roof Panel	Ceramitec Industries	60	58	02
2143 Brown Cement roof Panel	Ceramitec Industries	60	58	02

(Table 1) Contd…

Sample	Manufacturer	Temperature of Uncoated Panel (°C)	Temperature of Coated Panel (°C)	Temperature Difference (°C)
4231 Brown Cement roof Panel	Ceramitec Industries	60	54	06
2261 Black Cement roof Panel	Ceramitec Industries	60	59	01
431515C Black Cement roof Panel	Ceramitec Industries	60	61	- 01
43205 Black Cement roof Panel	Ceramitec Industries	60	56	04
1GY95 Black Cement roof Panel	Ceramitec Industries	60	57	03
161515 Black Cement roof Panel	Ceramitec Industries	60	60	00
6012 Green Cement roof Panel	Ceramitec Industries	60	55	05
23112 Green Cement roof Panel	Ceramitec Industries	60	55	05
(Undisclosed composition)D Cement roof Panel	Ceramitec Industries	60	51	09
(Undisclosed composition) K Cement roof Panel	Ceramitec Industries	60	51	09
Violet Fine (2% Loading) (Mica coated pigments) Cement roof Panel	Sudarshan Chemicals Pune, India	60	55	05
Violet Fine (25% Loading) (Mica coated pigments) Cement roof Panel	Sudarshan Chemicals Pune, India	60	49	11
Silver Fine (2% Loading) (Mica coated pigments) Cement roof Panel	Sudarshan Chemicals Pune, India	60	58	02

(Table 1) Contd…

Sample	Manufacturer	Temperature of Uncoated Panel (°C)	Temperature of Coated Panel (°C)	Temperature Difference (°C)
Silver Fine (25% Loading) (Mica coated pigments) Cement roof Panel	Sudarshan Chemicals Pune, India	60	49	11
Silver Fine (50% Loading) (Mica coated pigments) Cement roof Panel	Sudarshan Chemicals Pune, India	60	41	19
Aluminum Paste Cement roof Panel	Sudarshan Chemicals Pune, India	60	46	14
Hi Tech Red Coating Cement roof Panel	Hi Tech	60	54	06
Hi Tech White Coating Cement roof Panel	Hi Tech	60	46	14
Hi Tech Green Coating Cement roof Panel	Hi Tech	60	54	06

All the pigments listed above are inorganic pigments obtained from different manufacturers. They contain different components and are of different particle sizes. Most of these pigments have shown good IR reflectivity. Some of the pigments having the similar composition have shown different reflectivity.

Another method to determine the infrared reflectivity of pigments is Drift Infrared Spectroscopy. The samples were analyzed by Perkin Elmer Spectrum One NTS system. This technique is able to accurately measure the infrared reflectivity with little or no sample preparation. It is also versatile and fast and can be used for wide range of samples. Figs. **3** and **4** show the drift infrared spectra of Synthetic Rutile (enriched ilmenite by reduction and acid treatment to remove iron) obtained from CMRL. These pigments have crystal structure same as that of rutile titanium dioxide containing traces of iron. These pigments have shown good reflectivity in the wavelength of 700 to 2400 nm.

CURRENT & FUTURE DEVELOPMENTS

Industry has realized the potential of these pigments and products for refrigerated transport containers, roofs of the buildings are already in use. Further use of these coatings in petroleum refinery to reduce evaporation losses of hydrocarbons is being explored. Published information on preparation of these pigments is not available. It is expected that a good deal of research may be published in coming years. We have found from our tests that there is no known method to predict the infrared reflectivity of any substance. The only technique to find out if a pigment reflects infrared radiations is to test its reflectivity. Any specific physical property of the pigment cannot be correlated with its infrared reflectivity. Like other physical properties of matter such as density, transparency or opacity, refractive index, color, thermal conductivity, electrical conduction or resistance, semi conductivity there is no method to predict the infrared reflectivity of a substance. It should be possible to screen a large number of inorganic pigments manufactured by several manufacturers world over to look for IR reflecting pigments. Organic pigments , which are relatively simple to synthesize and are far more explored could be screened for their IR reflectivity. Only one compound of about 100 synthesized qualifies for a commercial pigment. There are thus thousands of products that need to be studied for their IR reflectivity. The starting point is chlorophyll. Collaborative research programs between physicists, organic chemists and paint technologists are more likely to yield results.

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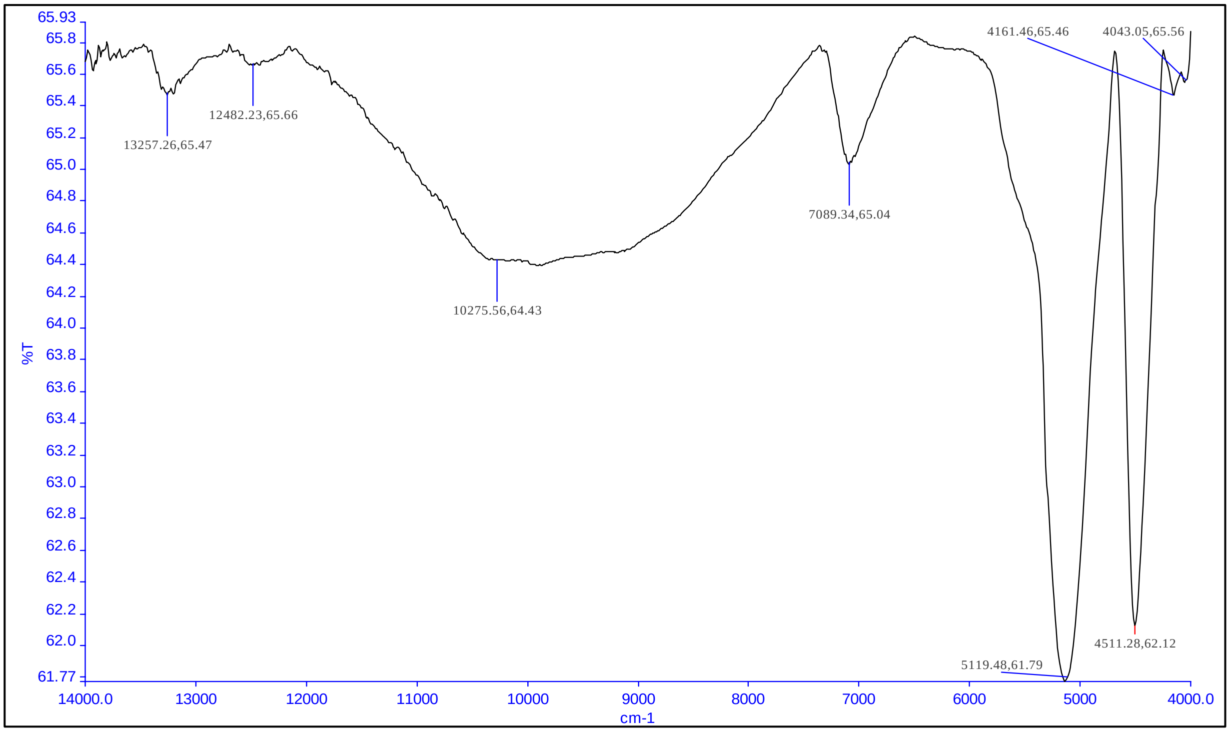

Fig. (3). Drift IR Scan of Synthetic Rutile (Enriched Ilmenite) Sample.

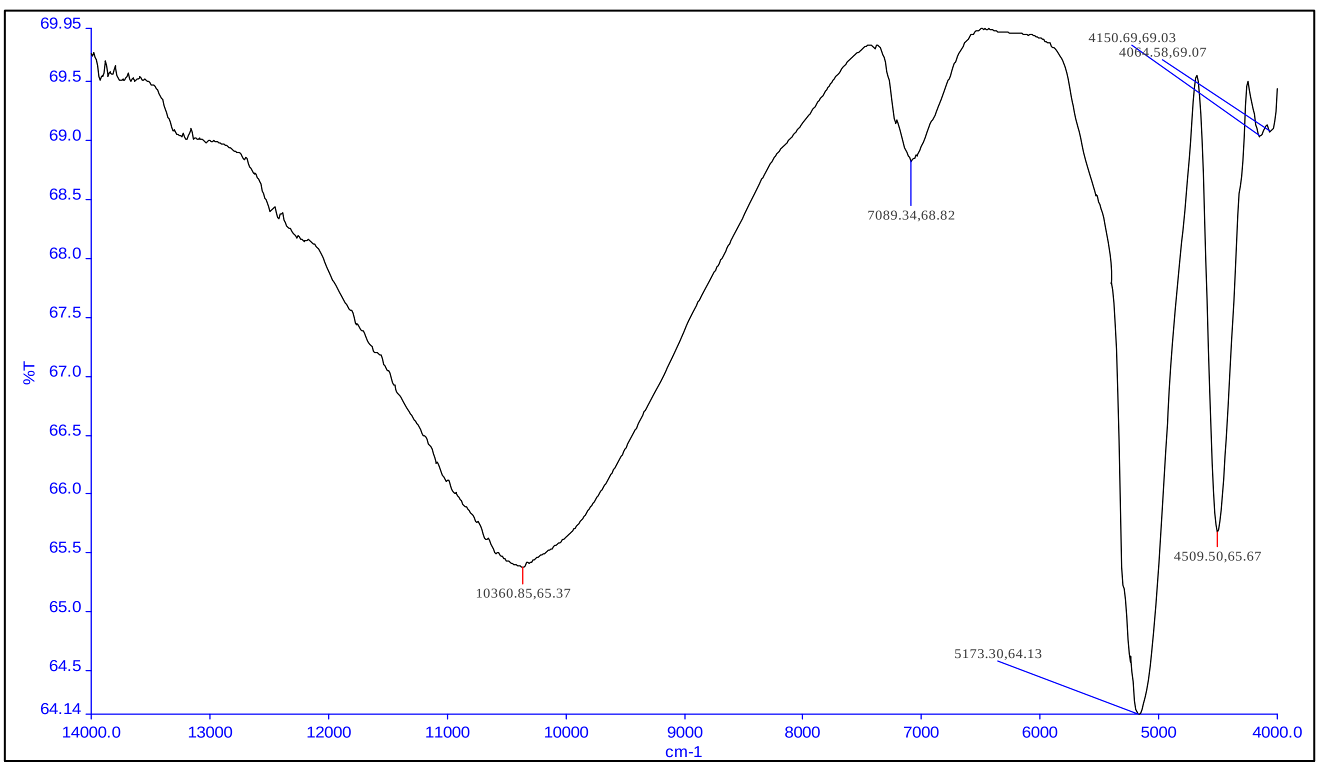

Fig. (4). Drift IR Scan of Synthetic Rutile (Hydrated Titanium Dioxide) Sample.

4. Shepherd Color Company, 4539 Dues Dr., Cincinnati, OH 45246-1006, USA for a liberal supply of the entire range of their IR reflecting products

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