

UNIQUE RARE EARTH PIGMENTS FOR MORE THERMALLY COMFORTABLE LEATHERS

by

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ABSTRACT

This paper reports the investigations carried out on the synthesis, characterization and optical properties of a new class of rare earth based near infrared reflective yellow pigments as an alternative to toxic inorganic pigments. The rare earth yellow pigments can be prepared by employing calcination method. The present work reveals that the doping of molybdenum for ceria in gadolinium cerium lattice changes the color hue from cream white to dark yellow. The calcination temperature employed for preparation of these pigments was about 1000°C. This temperature was found to be much lower than that required to achieve the intense yellow hue through conventional solid state calcinations reaction (above 1500°C). X-ray diffraction data confirm the crystalline character of the pigments. The pigment thus developed serves as a potential candidate for NIR reflective pigments for leather applications on account of its NIR reflectance value of 96% in the wavelength region 1100 nm. Thermal images of the finished leather exposed to NIR light clearly indicate the lower heat retention character. The pigment properties were in good agreement with industrial requirements. They also serve as environmentally safer pigments.

INTRODUCTION

Modifying the leather finish formulations in such a manner that the customer preferences are met effectively has been one of the major goals of leather researchers. The temperature of leather, whether it is used to upholster automobile or to manufacture garments worn in tropic conditions is an important comfort parameter modifiable using finish formulations. Leather can reflect or absorb solar energy from UV, visible or infrared regions. Forty-five percent of the total solar energy being in the infrared region,¹ the ability of leather to reflect near infra-red radiations (NIR) determines the comfort factor from leather employed as upholstery or garments. A significantly large number of pigments employed in leather finishing such as carbon black, iron oxide black etc have very low total solar reflectance. This brings in a precarious situation where a material (skin) with inherently high solar reflectance, loses the same on conventional finishing. Further, very few colours used in leather finishing are single pigment dispersions. In order to match a colour, more than one pigment is mixed together and the combined pigment is reported to have lower total solar reflectance than the weighted average of individual pigments. In addition to the comfort properties, there is also a need to relook into the types of pigments employed in the industry.

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The pigments for specialty coloring are usually inorganic products composed of metal oxides as they possess thermal and chemical stability at high temperature and are inert to the chemical action from perspiration etc. Although PbCrO_4 , PbMoO_4 , $\text{Pb}_2\text{Sb}_2\text{O}_7$ and CdS have been widely employed as conventional yellow pigments, the use of these pigments has been restricted because they contain toxic elements.^{2,6} Thus serious need arises to identify environmentally friendly and economically viable materials to replace toxic inorganic pigments. Incidentally, these properties are difficult to achieve with organic pigments, where transparent character along side high fastness to light and weathering is required, leading insufficient color range and pigments which can cover defects. Among the inorganics, praseodymium yellow has been known as one of the environmentally benign yellow pigment that has been applied for many surface coating applications.^{4,6} Recently several rare earth based yellow pigments have been proposed as viable alternatives to existing traditional toxic pigments by many researchers, including from our group.⁷⁻¹⁰ This is because lanthanide ions have unique optical properties.¹¹⁻¹⁵ The electronic configuration of the valence layer of the trivalent lanthanide ions $[\text{Xe}] 4f^n$, involves the activity of internal f electrons strongly shielded by $5s$ and $5p$ electrons, with the result that the crystalline field caused by the interaction with neighboring ions is very low. This leads to optical spectra of lanthanide compounds usually presenting weak and profuse bands. This phenomenon offers a wide scope for the designing of colorants for specific applications.¹⁶ Some of the rare earth yellow pigments reported recently such as mixed oxides of yttrium- molybdenum, samarium-cerium-molybdenum, barium-tin-tantalum and cerium-zirconium-tantalum have shown excellent hue. The main drawback of these pigments is that the synthetic process of most of these pigments involves either the use of toxic chemical inputs or high-energy reactions. New directions, such as use of a benign hydrothermal route to obtain brilliant yellow colored bismuth vanadate (BiCaZnVO_4) has been reported.¹⁷ Among the rare earth components in the mixed metal oxide pigments, the use of cerium has been more common as it is a known ultraviolet blocker.¹⁸ The coloring mechanism is based on the charge-transfer band from O_{2p} to Ce_{4f} in the semiconducting CeO_2 .¹⁹ The band gap between the anionic O_{2p} valence band and the cationic Ce_{4f} conduction band can be modified by the formation of solid solutions, which introduces an additional electronic level between the valence and the conduction band.¹⁰ Cerium oxide is a fluorite-structured oxide that can form extensive solid solutions with a variety of alien cations while retaining the fluorite structure. The present research work has been undertaken to investigate the effect of molybdenum doping on the color and covering of gadolinium cerium oxide pigments. The pigments have been prepared by employing calcination route. The resultant oxides have been characterized by XRD, SEM, UV-Vis NIR spectroscopy and CIE Lab 1976 color co-ordinates. The application of these pigments in surface coating of leather is highlighted here.

MATERIALS AND METHODS

Materials

Gadolinium (III) chloride hexahydrate (>99% purity) [CAS No 13450-84-5], and Ammonium heptamolybdate tetrahydrate (99% purity) [CAS No 12054-85-2] were procured from M/s. Sigma Aldrich. Cerium (III) chloride hydrate (99.9% purity) [CAS No 19423-76-8] was procured from M/s. Alfa Aesar.

Synthesis of Yellow Pigment

Pure and molybdenum doped gadolinium cerium oxide was prepared by conventional solid state route. $\text{Gd}_1\text{Ce}_{1-x}\text{Mo}_x\text{O}_{3.5+Y}$ ($X=0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35$) in appropriate mole ratios of Ce, Gd and Mo salts were well homogenized (thorough mixing using a mortar and pestle) and calcined in an electrically heated furnace (chamber - w x h x d = 150 x 150 x 200 mm) at 1000°C for a duration of 2 h. The rate of heating up to 250°C was maintained at 15°C/min and subsequently reduced to 5°C/min. The obtained powder was cooled naturally, homogenized in a mortar with a pestle and characterized.

Size Evaluation

Dynamic light scattering (DLS) measurements were performed on a Malvern Instruments Zeta Sizer 3000 HSA, using a He-Ne laser (633 nm), at a scattering angle of 90° and at 25±1°C. The mean hydrodynamic diameter of the particles was obtained using the software provided by Malvern Instruments. The NNLS (Non-negative least square routine) model was applied to obtain the size data.

Phase Purity

Powder X-ray diffraction measurements were carried out using a Rigaku Multiflex instrument using a Ni filtered $\text{CuK}\alpha$ radiation with $\lambda = 0.154060$ nm source and a scintillation counter detector in the 2θ angle range of 10° – 80° with step size of 0.1°. XRD pattern were compared with the JCPDS reference data for phase identification.

Surface Morphological Analysis

Electron microscopic studies were done on a JEOL JSM 5600-LV microscope with an accelerating voltage of 20kV. The quantitative microanalysis of the products was carried out by energy dispersive spectrometer (EDAX, USA).

Optical Characteristics

A Shimadzu UV-3600 UV-Vis-NIR spectrophotometer along with a diffuse reflectance accessory (DRA) was used to measure reflectance properties of the pigments. DRA was capable of measuring reflectance in the region of 250 – 2500 nm. In the present study, the DRA was operated in the diffuse reflectance mode in the region of 700 – 2500 nm, at 5 nm interval. Reflectance was measured as relative, defined as the ratio of flux reflected by the specimen to the flux reflected by a reference surface. Polytetrafluoroethylene (PTFE) was used as the reference.

Preparation of Finishing Formulation

The prepared yellow pigment was used as a pigment in leather finishing. Every 100 g of finishing formulation consisted of 16.0 g of soft resin binder; 10.5 g of medium soft resin binder; 13.0 g of protein binder; 7.5 g of polyurethane binder; 5.5 g of wax emulsion; 6.5 g of pigment; 3.0 g of iso-propyl alcohol and 38 g of water. The prepared finish formulation was applied on white crust leather for evaluation.

Characterization of Finished Leathers

Finish adhesion test was performed as per SATRA standards 112 (Method SLF 11). The light fastness of the finished leather was determined by SATRA TM 160 and that of rub fastness by SATRA TM 167. Organoleptic properties were evaluated by three experienced tanners in a scale of 0 – 10. The thermal image of NIR reflective pigment coated leather samples were evaluated by means of IR and visible systems [FLIR system E60] having a thermal sensitivity of $< 0.05^{\circ}\text{C}$ with a measurement range of -20°C to $+650^{\circ}\text{C}$ and an imager with a resolution of 320 X 240 pixels. The screen was observed from a distance of 30 cm at 25°C , 50% relative humidity. Reflectance measurements were carried out using a Milton Roy color mate HDS instrument. Color coordinates (L, a^* , b^* , h and C) were recorded and the total color difference (ΔE) and hue difference (ΔH) were calculated using the following equations:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (1)$$

$$\Delta H = \sqrt{\Delta E^2 - \Delta L^2 - \Delta C^2} \quad (2)$$

Where ΔE = overall color difference; ΔL = Lightness difference; Δa and Δb = difference of a and b values, where 'a' represents the red and green axis and 'b' represents the yellow and blue axis; ΔH , hue difference, ΔC , chromaticity difference.

RESULTS AND DISCUSSION

Powder X-Ray Diffraction Analysis

XRD patterns of cerium gadolinium oxide with 0.05 to 0.35 mol% Mo doping are shown in Figure 1. The intense and sharp peaks found in the diffraction pattern reveal the crystalline nature of the phase. The evaluation of the position of main reflections corresponding to (111) (200) (220) (311) was carried out and found to be in accordance with the data in the JCPDS card no 34-0394 of a cubic fluorite structure of CeO_2 with a space group Fd_3m . Gd atoms substitute cerium atoms in their crystal lattice forming uncharged substitution defects. The formation of these defects is associated with decrease in the volume of elementary unit cell. No separate phase corresponding to gadolinium oxide could be found indicating intimate mixing of cerium and gadolinium ions in the precursors. Thus gadolinium enters into cerium oxide fluorite forming $\text{CeO}_2\text{-Gd}_2\text{O}_3$ solid solution. With increasing

molybdenum doping, peaks corresponding to molybdenum oxide [#] phase alongside those of CeO_2 phase [*] appear in the diffraction pattern, which is in agreement with JCPDS card no 89-6725. The crystallite size calculated using Debye Scherer formula was found to be in the range of 16 nm to 22.50 nm.

Particle Size and Morphological Analysis

The physical characteristics for inorganic pigments comprise not only optical constants but also geometric data such as mean particle size and particle shape. Particle size analysis of gadolinium cerium molybdenum oxide [Gd: Ce: Mo = 1:0.65:0.35] shows an intensity average diameter of 832 nm. The SEM micrograph of 0.35 mol% Mo doped gadolinium cerium oxide is shown in Figure 2. SEM image shows homogeneous and spherical morphology. E-dax analysis confirmed the presence of all expected elements.

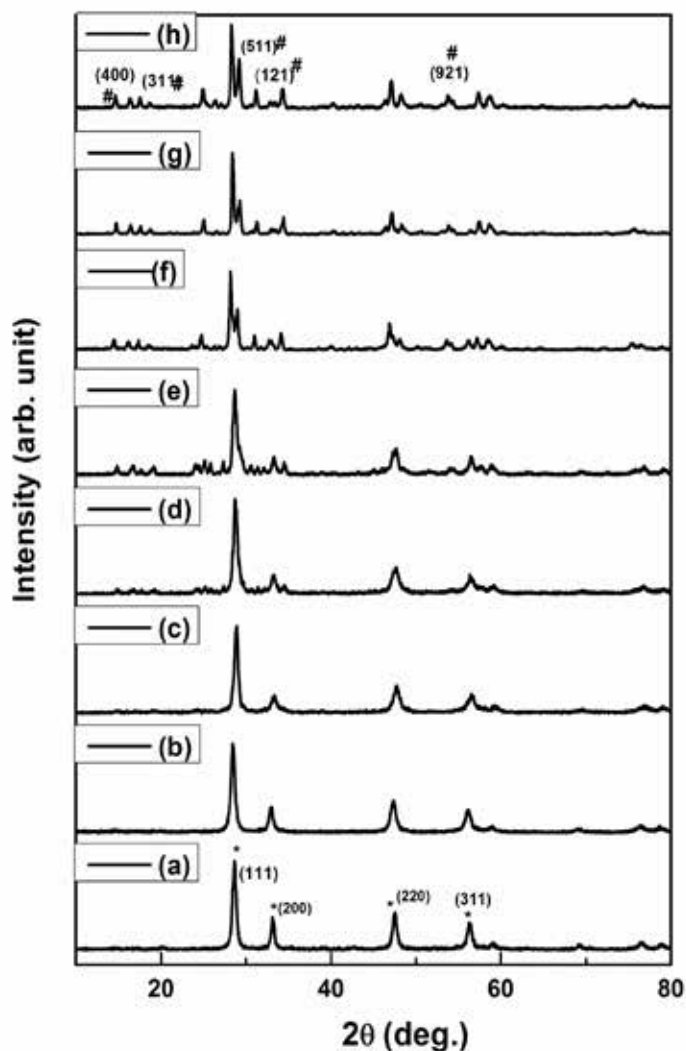


Figure 1. XRD of Gd:Ce:Mo at a) [1:1:0] b) [1:0.95:0.05] c) [1:0.9:0.1] d) [1:0.85:0.15] e) [1:0.8:0.2] f) [1:0.75:0.25] g) [1:0.7:0.3] h) [1:0.65:0.35].

Near Infra-Red Reflectance of Leather

A NIR reflective pigment is one which has lower absorbance and high reflectance. Intense solar radiation can potentially raise temperature of the leather surface, leading to discomfort while traveling in convertibles with such upholstery and also increased costs for rapid cooling of the vehicle interior. The use of highly reflective pigment helps in maintaining a lower leather surface temperature and consequently contributes to reduced energy costs for cooling, similar to the case of roof top coatings of buildings.^{20,21} Solar radiation consists of 5% UV radiation, 43% visible radiation 52% NIR radiation.²² Coatings colored with conventional pigments tends to absorb NIR radiation that bears >50% of the power in the sunlight resulting in heat build-up.^{23,24} NIR reflectance spectra of leather coated with the pigment prepared in this study is shown in Figure 3. The NIR reflectance spectral value of conventional inorganic yellow pigments such as cadmium yellow pigment, nickel titanate yellow, iron oxide yellow is reported to be 87, 77 and 70% respectively.²² In the case of the leather finished using the pigment prepared in this study, a NIR reflectance value of 96% was observed at 1100 nm. This enhanced value indicates the potential utility of these pigments for thermally comfortable leathers.

CIE Lab Color Coordinates

The chromatic properties of the powder pigments can be analyzed from their CIE LAB 1976 coordinates. Doping of Mo⁶⁺ for Ce⁴⁺ shows a significant increase in the b* and C. Hue value of molybdenum doped cerium gadolinium oxide pigment also lies in the yellow region of cylindrical color space (h=70-105 for yellow). With doping of Mo⁶⁺ for Ce⁴⁺ from 0.05-0.1% a* value seems to be negative resulting in a greenish tint. Color coordinate values presented in Table I clearly outline the observed trend in tint change. The resultant pigment with 0.35 mol% Mo doping was employed in leather finishing [Figure 5b]. The color coordinates in three different regions, viz., butt, belly and neck are presented in Table II. The results clearly indicate uniform coating of the leather surface. The color coordinates have been compared against conventional cadmium yellow pigments and ΔE value was found to be around 10-12, indicating that the colors are close enough for comparison of thermal properties.

Effect of Light Fastness on Finished Leathers

The fastness characteristics of leathers to light and rubbing are given in Table III. The leathers from both control and matched pair experimental processes exhibit similar values that are equivalent to the Blue wool standards 4.5 (given in parenthesis in Table III). The prepared yellow pigments thus meet the standard norms.

Organoleptic Properties Assessed by Tactile Evaluation

Visual assessment data shown in Figure 4 clearly indicate no loss of properties on finishing with this pigment. The same has not been compared against any industrial standard (control pigment) due to variations in size and composition of the commercial vis-à-vis synthesized product.

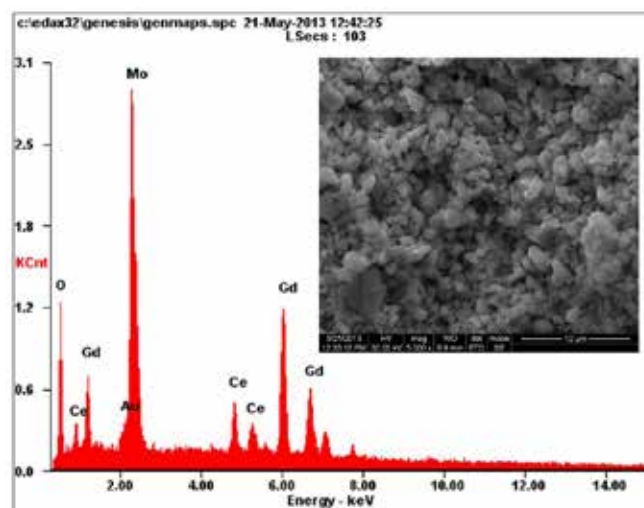


Figure 2. SEM- EDAX of {Gd: Ce: Mo [1:0.65:0.35]}.

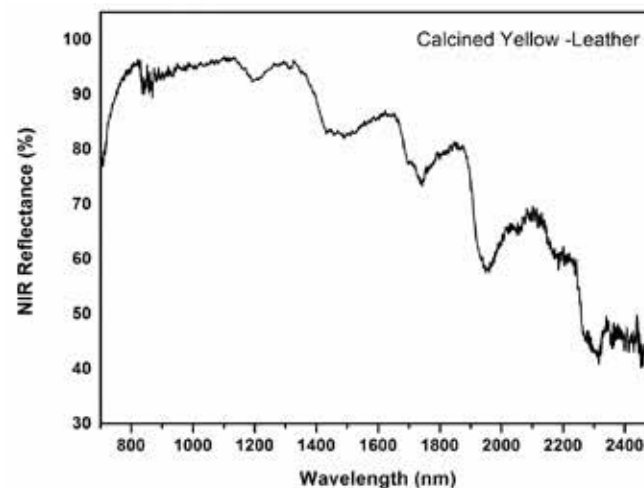


Figure 3. NIR-Reflectance of yellow leather {Gd: Ce: Mo [1:0.65:0.35]}.

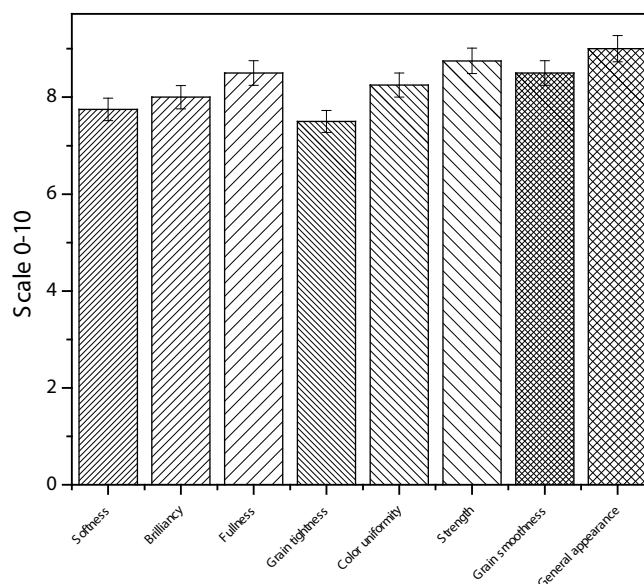


Figure 4. Visual assessment of finished leathers.

TABLE I
CIE lab colour coordinates
of yellow pigments.

Sample Gd: Ce: Mo	L	a*	b*	h	C
1:1:0	92.06	-3.55	6.21	119.76	7.16
1:0.95:0.05	90.08	-4.59	11.23	112.25	12.14
1:0.9:0.1	86.6	-2.58	13.71	100.67	13.95
1:0.85:0.15	87.36	-0.04	22.67	90.11	22.67
1:0.8:0.2	88.91	-3.46	26.44	82.53	26.66
1:0.75:0.25	83.87	7.3	34.04	77.89	34.81
1:0.7:0.3	82.44	8.7	42.04	78.3	42.93
1:0.65:0.35	80.66	10.67	47.94	77.44	49.11

Adhesion Test

In the finish formulation, either casein or resin binder is used to interact with leather to provide better bondage and film formation. However, the pigments will have interference in the binding capacity of finish film with leather. The yellow pigmented leather was tested for its adhesion efficiency by the adhesion testing method. The adhesion tests were carried out in dry and wet state. The leather in dry state shows strength of 5.1 N/cm and in wet state 1.15 N/cm, implicating the strong binding of finish film on leather.

Thermal Imaging of Leather

The thermal qualitative effect due to the presence of NIR reflective pigment coated leather can be evaluated by recording colour images using infrared thermal camera as shown in Figure 5. If no dyes or pigments are added, leather will reflect most of the IR radiation, which is responsible for the temperature increase at the surface. This means that an undyed crust is a material with very good solar reflectance. It can be assumed that this reflectance is due to the structure of the papillary layer, which will scatter and reflect the infrared radiation. Solar reflective leather will have greater extent reflect IR radiation due to its microscopic structure. When

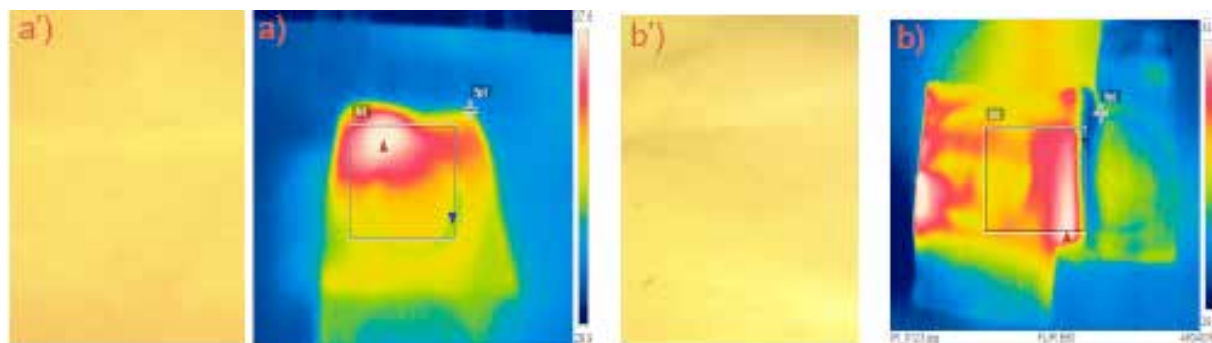


Figure 5. a) thermal image of conventional (cadmium yellow leather), a') photograph of the imaged surface, b) thermal image of experimental leather, b') photograph of the imaged surface of experimental leather {Gd: Ce: Mo [1:0.65:0.35]}(yellow leather).

TABLE II
Colour Measurements - Leather Surface.

Area	L	a*	b*	h	C
Butt	75.96 (71.18)	1.62 (1.50)	32.44 (41.42)	87.72 (73.56)	32.48 (53.55)
Belly	75.96 (72.31)	1.59 (1.58)	32.45 (43.77)	87.16 (73.62)	32.49 (56.04)
Neck	75.49 (69.14)	1.63 (1.64)	32.42 (40.47)	87.09 (72.01)	32.46 (53.06)

(values in paranthesis indicate those finished with cadmium yellow pigment)

TABLE III
Fastness to rubbing and light fastness.

Sample	After ageing		Light fastness ^a
	Wet rubbing	Dry rubbing	
Conventional	4.0 - 4.5	4.5 - 5.0	3.5-4.0
Gd: Ce: Mo	4.0 (4.0-4.5)	4.5 - 5.0 (4.0-4.5)	4.0-4.5 (4.5-5)

^avalue in parenthesis indicates the corresponding blue wool standard

exposed to IR light for 10 minutes, the surface temperature (32°C) of finished NIR reflective yellow leather Gd: Ce: Mo 1:0.65:0.35 was lower than the surface temperature (34°C) of conventional cadmium yellow leathers. Error factor is determined by the sharpness of image and according to the manufacturers the accuracy is $\pm 1^\circ\text{C}$. Thus difference in temperature (2°C) clearly indicates the potential utility of synthesized yellow leathers as thermally comfortable leathers. The enhanced cost due to the presence of rare earth metal ions is likely to be offset by the increased price per square feet of the value added leather.

CONCLUSIONS

It has been possible to utilize the environmentally benign NIR reflective pigments generated for leather coating purpose. With a reflectance of over 96% the yellow pigments serve as NIR reflective pigments for leather coating applications. The pigment also finds application in covering of surface with low pigment loading, retaining the aesthetics of the grain and improved levelness, excellent physical properties, ageing resistance and miscibility with water.

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REFERENCES

1. Green, A.C.; Premature aging of the skin in Queensland population. *J.Aust.* **155**, 413-478,1991.

- Trojan, M., Solc, Z., Novotny, M.; Kirk-Othmer encyclopedia of chemical technology, nickel and nickel alloys to paint and paint dispersing, New York: J. Wiley and Sons Inc. 17, 1995.
- Badenes, J.A., Liusar, M., Tena, M.A., Calbo, J., Monros, G.; Praseodymium-doped cubic Ca-ZrO₂ ceramic stain. *J.Eur.Ceram.Soc.* **22**, 1981-1990, 2002.
- Nero, G.D., Cappelletti, G., Ardizzone, S., Fermo, P., Gilardoni, S.; Yellow Pr-zircon pigments: the role of praseodymium and of the mineralizer. *J.Eur.Ceram.Soc.* **24**, 3603-3611, 2004.
- Hill, K., Lehman, R., Swiler, D.; Effects of selected processing variables on color formation in praseodymium-doped zircon pigments. *J.Am.Ceram.Soc.* **83**, 2177-2182, 2000.
- Blonski, R.P.; Stable heavy metal free zircon pigments for use in plastics and paints and method for coloring thereof. U.S. Patent 5,316,570, 1994.
- Prabhakar Rao, P., Reddy, M.L.P.; (TiO₂)(CeO₂)_{1-x}(RE₂O₃)_x-novel environmental secure pigments. *Dyes. Pigm.* **73**, 292-297, 2007.
- George, G., Sandya Kumari, L., Vishnu, V.S., Ananthakumar, S.; Reddy, M.L.P.; Synthesis and characterization of environmentally benign calcium-doped Pr₂Mo₂O₉ pigments: Applications in coloring of plastics. *J.Solid State Chem.* **181**, 487-492, 2008.
- Gauthier, G., Jobic, S., Evain, M., Koo, H.J., Whangbo, M.H., Fouassier, C.; Synthesis structures and optical properties of yellow Ce₂Si₃, Ce₆Si₄S₁₇ and Ce₄Si₃S₁₂ materials. *Chem.Mater.* **15**, 828-837, 2003.
- Sreeram, K.J., Radhika, S., Devi, J.M., Nair, B.U., Ramasami, T.; Cerium Molybdenum Oxides for environmentally benign pigments. *Dyes. Pigm.* **75**, 687-692, 2007.
- Taniguchi, H., Kido, J., Nishiya, M., Sasaki, S.; Europium chelate solid state laser based on morphology-dependent resonances. *Appl. Phys. Lett.* **67**, 1060-1062, 1995.
- Bunzli, J.C.G.; Piguet, C.; Taking advantage of lanthanide luminescent ions. *Chem. Soc.Rev.* **34**, 1048-1077, 2005.
- Kido, J., Okamoto, Y.; Organo lanthanide metal complexes for electroluminescent materials. *Chem. Rev.* **102**, 2357-2368, 2002.
- Biju, S., Reddy, M.L.P., Cowley, C.H., Vasudevan, K.V.; 3-Phenyl-4-acyl-5-isoxazolonate complex of Tb³⁺ doped into poly-β-hydroxybutyrate matrix as a promising light-conversion molecular device. *J. Mater. Chem.* **19**, 5179-5187, 2009.
- Buxbaum, G., Pfaff, G.; Industrial inorganic pigments. 3rd ed. Weinheim: Wiley-VCH. 2005.
- Bunzli, J.C.G., Andre, N., Elhabiri, M., Muller, G., Piguet, C.; Trivalent lanthanide ions: Versatile co-ordination centers with unique spectroscopic and magnetic properties. *J. Alloys Compd.* **303**, 66-74, 2000.
- Masui, T., Honda, T., Wendusu, Imanaka, N.; Novel and environmentally friendly (Bi, Ca, Zn) VO₄ yellow pigments. *Dyes. pigm.* **99**, 636-641, 2013.

18. Singh, S., Dosani, T., Karakoti, A.S., Kumar, A., Seal, S., Self, W.T.; A phosphate-dependent shift in redox state of cerium oxide nanoparticles and its effect on catalytic properties. *Biomaterials* **32**, 6745-6753, 2011.
 19. Chuang, C.C., Chen, M.J., Hsiangw, H.I., Yen, F.S.; Effect of Ba²⁺ addition on phase separation and oxygen storage capacity of Ce_{0.5}Zr_{0.5}O₂ powder. *J.Am.Ceram.Soc* **94**, 895-901, 2011.
 20. Baneshi, M., Maruyama, S., Nakai, H., Komiya, A.; A new approach to optimizing pigmented coatings considering both thermal and aesthetic effects. *J. quant.spectrosc. Radiati transfer*. **110**, 192-204, 2009.
 21. Uemoto, K.L., Sato, N.M.N., John, V.M.; Estimating thermal performance of cool colored paints. *Energ. Buildings*. **42**, 17-22, 2010.
 22. Levinson, R., Berdahl, P., Akbari, H.; Solar spectral optical properties of pigments-part II: Survey of common colorants. *Sol. Energy Mater. Sol Cells*. **89**, 351-389, 2005.
 23. Vishnu, V.S., Reddy, M.L.P.; Near-infrared reflecting inorganic pigments based on molybdenum and praseodymium doped yttrium cerate: synthesis, characterization and optical properties. *Sol. Energy Mater. Sol Cells*. **95**, 2685-2692, 2011.
 24. Sreeram, K.J., Aby, C.P., Nair, B.U., Ramasami, T.; Colored cool colorants based on rare earth metal ions. *Sol. Energy Mater. Sol Cells*. **92**, 1462-1467, 2008.
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