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Use of mixed rare earth oxides as environmentally benign pigments

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Abstract

A new class of environmentally benign brown rare earth colorants as alternatives to toxic inorganic colorants is presented. These colorants are based on mixed rare earth oxides. Unique feature of these colorants is the utilization of mixed rare earth oxides after the removal of radioactive thorium from monazite sand. The utility of mixed rare earth oxides for general exterior coating applications has been evaluated through mass tone/hiding power evaluations and the product has been fine tuned with respect to particle size, combination with hydrophilic agents, binders etc. to achieve good hydrophobicity and covering on porous surfaces like leather. The pigment was compatible with various auxiliaries employed in leather finishing and meets the current requirements for pigments like upgrading of finished leather through excellent covering of surface and improved levelness, no overloading of grain, excellent physical properties, ageing resistance and miscibility with water.

Keywords: Environmentally benign pigments; Mixed rare earth oxides; Leather; photoacoustic spectroscopy

1. Introduction

The need to replace cadmium and lead pigments in surface coating applications, especially for colors like red and yellow has received wide focus in recent years [1]. In the leather industry itself, currently employed pigments such as lead molybdate, cadmium sulfoselinide etc. have to be phased out [2]. The rare earth elements offer a vast opportunity for developing environmentally secure alternatives. Rare earths, because of their unique electronic configuration of partially filled f orbital, show unusual magnetic and optical properties [3]. Many trivalent lanthanide ions are strikingly colored both in solid state and in aqueous solutions. The color developed depends on the number of unpaired electrons. The pigments derived from rare earths show their characteristic intense color due to charge transfer interactions between a donor and an acceptor with the metal ion playing generally the role of an acceptor. Selection of rare earth elements and appropriate donor atoms for achieving the best spectral bandwidth and intensity forms the leading edge of knowledge in this area. Dopants based on rare earth elements in mixed oxide systems offer opportunity to tune in color response through manipulation of energy gaps and delocalization phenomena in conduction and valence bands [4].

Separation chemistry is central to many of the most successful uses of rare earths. For the rare earths, two distinct separations are important: (1) separation of the rare earths as a group from the matrix elements, and (2) separation of the individual members of the series. Due to the chemical similarities of the rare earths and the existence of these metal ions in essentially one oxidation state, the latter is one of the greatest challenges in the separation of metal ions and this in turn makes the use of the rare earth salts economically constrained [5]. It is in this context that the use of mixed rare earth salts (after separation of rare earths as a group from the matrix (monazite, in the Indian context)) for various applications including those of colorants becomes relevant. Leather industry is one amongst the industries which rely on colorants extensively. There are barriers to trade in this industry that are

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exclusively based on the presence of harmful chemicals in the leather or leather product.

Leather industry worldwide is undergoing major changes. The enormous scope for improving all stages of the manufacturing process from the point of view of ecology has been recognized. Paradigm shifts from chemical to bioprocessing of leather is gaining relevance [6]. There is a need to couple utility value with the fashion and economic value of the leather product. For this, the tanner has to present the leather in the most desirable form, for which the natural blemishes are to be hidden through finishing. The list of problems currently affecting finishing products is continuously increasing. There are legislations which are in vogue in several countries, especially in US and Europe, which call for either a ban or limited use of several chemicals. For instance, this includes heavy metal ions like chromium, lead, cobalt and nickel in the pigment coat, alkyl tin compounds, alkylphenolethoxylates, *N*-methylpyrrolidone, residual formaldehyde and hazardous reactive crosslinkers in finish formulations [2]. It is in this direction, that an alternative safer pigment to the conventional pigments is desirous. Most of the leathers are colored to black and brown. This paper reports the development of a brown colored pigment based on rare earth salts. Pigments based on CeO_2 are inorganic colorants with high temperature stability and in the orange–pink hue when doped with praseodymium [7]. Lanthanum oxide (La_2O_3) and praseodymium dioxide (PrO_2) dissolve in cerium oxide at 1300 °C forming a solid solution of the three oxides. CeO_2–PrO_2–La_2O_3 pigments give very interesting red hues in the ceramic glaze. These heat and chemical-resistant pigments have a fluorite structure and represent potential environmentally friendly inorganic colorants [7]. However, the cost of separation of the rare earth metal ions owing to their similarities in properties has made these pigments not so economically viable. It is in this context that this paper reports the use of mixed rare earth oxides as viable alternative. Mixed rare earth oxides are derived from monazite sands in India after the separation of radioactive materials like thorium.

2. Materials and methods

2.1. Mixed rare earth oxides (REO)

Mixed rare earth oxides were sourced from M/s. Indian Rare Earths Limited, Alwaye, India. The material is obtained by high temperature calcination of mixed rare earth carbonates obtained after the separation of radioactive elements like thorium from monazite sand. The composition of the mixed rare earth oxides was evaluated by ICP analysis. The oxide was pulverized in a ball mill and separated into compositions with >63 µm , 63–45 µm, <45 µm and <25 µm for further studies. The photoacoustic spectrum of the pigment was analyzed. The photoacoustic spectrophotometer employed in this work consisted of a 450 W Xenon lamp (Jobin Yvon), an electromechanical chopper (PAR 650), a lock-in amplifier (Perkin Elmer 7225 DSP) and the PA cell made of stainless steel. The experimental setup is explained elsewhere [8]. For the photoacoustic measurement, the pigment powders were pelletized to about 4 mm diameters and placed inside the photoacoustic cell. An electromechanical chopper chops white light from the Xenon lamp and the chopped beam falls on the sample inside the cell. The diameter of the light spot incident over the sample is around 0.3 cm. Light is absorbed on the surface of the sample. The microphone in the PA cell detects the photoacoustic signal generated. The microphone is placed behind the sample, so that only transmitted waves are detected. This is then fed to a lock-in amplifier where the readings are recorded.

2.2. Mass tone/hiding power of the pigments

The pigments ground and separated to various sizes were analyzed for their mass tone/hiding power. For this a standard commercial paint composition consisting of a long oil alkyd, dispersing agents and mixed drier was employed. Mineral turpentine was used as the medium. The hiding power was evaluated by coating on an opacity chart at a thickness of 150 µm. The CIELAB 1976 method of determination of L, a^* and b^* was employed to determine the hiding power of the pigments by comparison of values when coated on white as against that on a black patch.

2.3. Evaluation of role of pigment to binder ratio on the stability of the emulsion

The REO of optimal particle size for covering was mixed with binder and an emulsion formulated with 10 g of REO, 4, 6, 8 g of a protein binder, 0.1 g of a commercial anionic wetting agent and 10 ml of water. The formulation was milled for 6 h and evaluated for its stability with time visually. For coating onto leather, the prepared finish formulation was coated with help of a commercial spraying device. Unless mentioned, two cross coats were given on the leather.

2.4. Evaluating the role of milling of dispersion on the stability of the emulsion

The formulated emulsion prepared from REO of optimal particle size and REO to binder ratio was milled for varying duration of time (8–32 h) and the stability of the emulsion evaluated both visually and through zeta potential measurements in a Malvern Zetasizer 3000 HSA.

2.5. Evaluating the role of coating of pigment particles with hydrophilic products to enhance dispersion and stability of the formulation

The pigment particles were coated using hydrophilic agents like polyvinyl alcohol (PVA), sulfated castor oil (SCO) and polyacrylic acid (PAA) at varying quantities (10:4 to 10:10) and milled for 8 h. The coated REO was then mixed with binder and other components of the emulsion (as in Section 2.3) and the prepared dispersion was evaluated for its stability and coating characteristics.

Table 1
Formulations evaluated for leather finishing

Component	Parts of emulsion			
	1	2	3	4
Pigment (coated)	10	10	10	10
Soft binder	40	0	0	0
Medium binder	0	40	0	0
Hard binder	0	0	40	0
Protein binder	5	5	5	5
Micro binder	0	0	0	40
Wax emulsion	2.5	2.5	2.5	2.5
Ammonia	0.5	0.5	0.5	0.5
Water	42	42	42	42

Two, three and four cross coats were made and the coated leathers evaluated for adhesion, light fastness and rub fastness.

2.6. Role of nature of binder

Formulations generally employed by the leather industry for finishing employ a combination of binders and other auxiliaries for finishing. This includes binders, feel modifiers etc. The formulations evaluated are presented in Table 1.

2.7. Evaluating the rub fastness and polarity of the coated leathers

The static contact angles for hexane and water (HPLC grade) were estimated on the leather samples using a goniometer telescope (home built). Each contact angle measurement was recorded within the first 10–20 s after slowly placing the sessile drop over a fresh surface region and repeated for reproducibility [9]. All measurements were made with the liquids equilibrated at 20 °C and 60% relative humidity. All the liquids used in contact angle measurements were of high purity and behaved reliably, and all leathers examined by the contact angle method were investigated at least in duplicate using independently prepared samples. The measured contact angles were reproducible within 1°. The rubbing test examines whether natural leather is well- or poor-finished during the process. At first, the finished leather is fixed on the rubbing tester and then, a small size of species wrapped with a white cloth was rubbed on the leather repeatedly ten times. After that, on estimating the amount of pigments that stained in the rubbed cloth, the rubbing effect is evaluated by applying it to the grey scale [10].

3. Results and discussion

The mixed rare earth oxide had a typical brown color. The composition and color coordinates as measured by CIELAB 1969 of the same is presented in Table 2. The photoacoustic spectrum of the REO is presented in Fig. 1. The spectrum presents various d–f and f–f transitions which are contributions of the various rare earth ions present in the mixed oxide. For instance, the signal around 400–450 nm could be attributed to one of the $^3P_j \leftarrow {}^3H_4$ transitions [11]. The existence of a $4f^1$ electron in Ce^{3+} configuration [Xe] $4f^15d6s$ markedly affects the electronic spectra of the ion. The ground state is the $^2F_{7/2,5/2}$ state, and the first excited state configuration is [Xe]$4f5d^16s$, leading to the $^2D_{5/2,3/2}$ state. The strong absorption observed at around 460 nm is based on 4f–5d transition [12].

Table 2
Characteristics of REO

Cerium	Praseodymium	Neodymium	Lanthanum	*L*	*a**	*b**
20.2	5.8	5.4	15.5	63.5	29.1	47.6

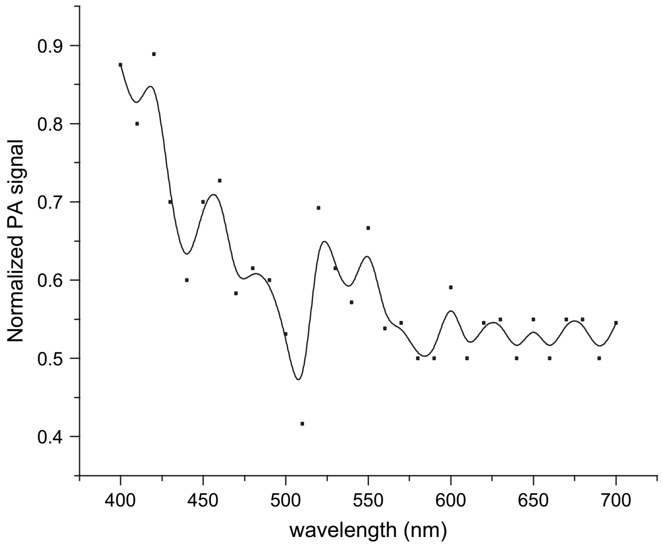
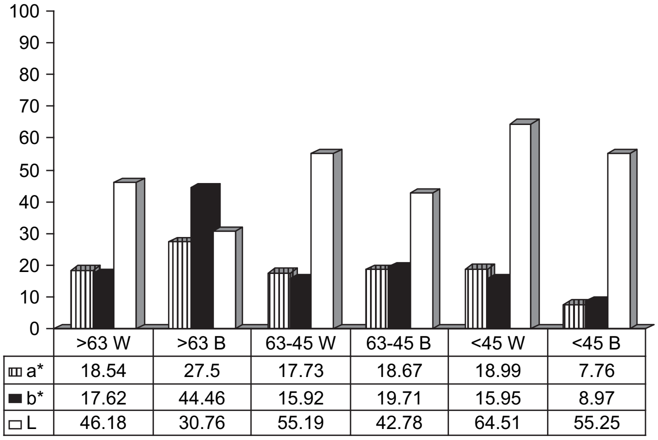


Fig. 1. Photoacoustic spectra of REO.

REO was hand ground and the mass tone or hiding power of the pigment was evaluated. Test methods for mass tone have been standardized as per procedures adopted by exterior coating (paint) industries. Results are presented in Table 3. A lower value of *a** and *b** on black as against white indicates that the black under layer of the opacity chart was not adequately covered. This is possibly because of a large number of particles of varying sizes being present in the sample. A better mass tone or covering power could be obtained by screening the particles to uniform size. The stability of the emulsion with time was evaluated visually and followed the order >63 μm <45–65 < 45 μm. The stability increased with decreasing particle size. In order to understand the role of particle size of the rare earth oxide based pigment particles in the mass tone of the dispersion, the particle size of the pigment after hand grinding which was in the range of 1100 μm were ball milled, reduced in size and were sieved to >63 μm, 63–45 μm and <45 μm, respectively and used for dispersing in the media. The mass tone was then evaluated. The results are presented in Fig. 2 (where W represents that on white, B on black). The variation in lightness factor *L*

Table 3
Covering power of REO

Condition	*L*	*a**	*b**	Δ*L* white vs black
On white	43.40	25.32	30.04	2.8
On black	40.60	17.33	23.87	



	>63 W	>63 B	63-45 W	63-45 B	<45 W	<45 B
▥ a*	18.54	27.5	17.73	18.67	18.99	7.76
■ b*	17.62	44.46	15.92	19.71	15.95	8.97
□ L	46.18	30.76	55.19	42.78	64.51	55.25

Fig. 2. Variation of mass tone with particle size.

between coating on white and black was of the order >63 μm (15.4) > 63–45 μm (12.4) > 45 μm (9.2), while that in the case of *a** and *b** was >63 μm > 45 μm > 63–45 μm. This indicates the need for lower particle sizes and of lower particle size distribution to enhance the hiding power of the pigments.

3.1. Role of pigment to binder ratio and milling on the stability of the emulsion

An emulsion was prepared as described in Section 2.3, employing REO and varying quantities of binder. The stability of the emulsion was evaluated visually as well as through zeta potential measurements. A zeta potential value of closer to zero indicates unstable emulsion, while a large negative potential indicates higher stability. The results presented in Table 4 indicate that a pigment to binder ratio of 1:0.8 was ideal with milling time of 8 h, while similar results are obtained only at 16 h for a 1:0.6 ratio. As duration of milling increases, the particles tend to reaggregate, indicating the relevance of milling duration on the stability of the composition.

The pigment dispersion process consists of wetting of pigment particles which are made up of agglomerates and aggregates, by immersing them in liquid/polymer, dispersant, surfactant solution followed by an input of mechanical energy to breakdown the agglomerates into primary particles and smaller aggregates. The primary particles consist of specific size aggregates and single crystals predetermined by pigment manufacturing process, in this case, the particles of >45 μm in size, to achieve a desired color and optical properties. Mechanical energy and good wetting by the solvent alone is not good enough to achieve stable dispersions. Generally stabilizing ingredient such as polymeric dispersant, dispersing resin or surfactant is required to avoid flocculation and reagglomeration of the dispersed phase. To obtain stable dispersion one must understand the predominant interactions between the pigment surface and solvent, the pigment surface and polymers and solvents. The dominant forces acting between particles govern stabilization. These forces consist of attractive ones called van der Waals forces and repulsive ones, either electric charges at pigment interfaces (charged double layer) and/or steric forces (polymer adsorption). All particles in void attract each other as a result of van der Waals forces. This attraction depends on the nature of particles, geometry and the medium used. It is independent of surface ions, pH and salt concentration. However, if a substantially greater repulsive force does not counteract this attractive force, the milled pigment dispersions will form flocculates and agglomerates on standing. To counteract the van der Waals attractive force between particles there are two repulsive forces consisting of electrostatic (DLVO) and steric forces (polymer adsorption). The mechanism is based on establishing charged double layer at particle liquid interface. It is primarily associated with aqueous systems. A charged species is preferentially adsorbed on the surface of particles producing a charged layer in the immediate liquid, with diffuse parts of the double layer extending far into the liquid. When two particles approach, the diffuse layers begin to interpenetrate, giving rise to strong columbic (electrostatic) repulsive force. The repulsive force increases in magnitude as the distance between the particle decreases. If the particles are forced to approach each other, the repulsive force can be surmounted with van der Waals attractive forces taking over and resulting coagulation of particles. Pigment dispersions only having charged double layer as stabilizing mechanism suffer from stability problems in pigment formulations due to pH changes, ionic concentration differences due to co-solvents and contamination by multivalent ions brought in by water during process. This brings in the need for steric stabilization.

Table 4
Effect of pigment to binder ratio and milling time on the stability of the emulsion

Pigment:binder ratio	Zeta potential (mV)			
	8 h	16 h	24 h	32 h
1:0.4	−2.2 ± 0.5	−2.9 ± 0.1	−3.2 ± 0.9	−5.6 ± 0.3
1:0.6	−3.2 ± 0.7	−6.4 ± 1.3	−6.2 ± 0.8	−4.2 ± 0.5
1:0.8	−6.2 ± 0.8	−8.2 ± 1.0	−6.2 ± 0.7	−6.2 ± 0.9

3.2. Role of hydrophilic agents on the stability of the emulsion

Steric stabilization is a repulsive mechanism based on adsorption of polymers on pigment surfaces. Steric stabilization accounts for counteracting the attractive forces (van der Waals) between particles in aqueous media for all polymers and dispersants. The repulsive forces are result of interpenetration of polymer tails and loops resulting in a restriction of number of conformations and decrease entropy as the two particles approach each other. There is a permanent barrier to irreversible changes even if the particles are further forced towards each other. This is only true for particles that have full surface coverage by polymers and these polymers stay adsorbed on the surface maintaining solvated tails. For high quality dispersions, steric stabilization is preferred mechanism in aqueous systems. The sterically stabilized dispersions are insensitive to salt concentration, shear and surface changes.

Table 5
Effect of REO: hydrophilic agent ratio on the physical characteristics of the finished leather

	Visual assessment[b]	Adhesion[b]	Wet rub fastness[b]	Dry rub fastness[b]	Light fastness[a]	γ_s^p (mN/m)
REO:PVA (1:0.4)	2	2/3	2	2	2	17.4 ± 0.2
REO:PVA (1:0.6)	2/3	2/3	3	3	2	14.6 ± 0.3
REO:PVA (1:0.8)	3	4	3	3	3	22.0 ± 0.1
REO:TRO (1:0.4)	2	2	2	2	2	16.3 ± 0.2
REO:TRO (1:0.6)	2	2	2	2	2	4.3 ± 0.4
REO:TRO (1:0.8)	2	2	2	2	2	5.0 ± 0.1
REO:TRO (1:1)	2	2/3	2	2	2	5.9 ± 0.4
REO:PAA (1:0.4)	2/3	2/3	2	2	2	5.9 ± 0.5
REO:PAA (1:0.6)	2/3	2/3	3	2/3	2	5.1 ± 0.2

[a] Grey scale reading.

[b] Evaluations carried out on a scale of 1–5 with 1 being poor and 5 being very good.

In order to determine the optimal ratio of pigment to hydrophilic agent required to bring about a complete coverage of the pigment particles, thus achieving a steric stabilization, the ratio of pigment to PVA/SCO/PAA was varied from 1:0.4 to 1:1. While PVA at ratio of 1:1 (REO:PVA) resulted in emulsions of high viscosity, which could not be used for coating purpose, PAA at 1:0.8/1.0 was unstable. γ_s^p vapor-to-water distribution coefficient is the highest for an REO:PVA ratio of 1.0:0.8, indicating that the leathers are more hydrophobic in character [13]. Undyed wetblue crusts were sprayed with four cross coats of the emulsion and evaluated. The results are presented in Table 5. It could be found from the results that an REO:PVA ratio of 1:0.8 was optimal, amongst the various options investigated.

3.3. Influence of number of cross coats on the properties of finish film

It is well known that when the number of cross coats increases, the covering power increases. However, this could also result in the loading of the grain and therefore poorer rub fastness. Results from this study indicate that four cross coats of an REO:PVA (1:0.8) emulsion was essential for wetblue undyed crust. The colors observed with varying cross coats and the properties observed are presented in Table 6.

3.4. Influence of nature of binder on the properties of finish film

The influence of binder (soft, medium, hard and micro) on the finish film characteristics is presented in Table 7. The microbinder due to the lower size provides for a higher b^* value and is also more hydrophobic in character. Industrial experts have evaluated the finished leathers as comparable to conventional leathers.

Table 6
Effect of number of cross coats on the finish film characteristics

Parameter	Two cross coats	Three cross coats	Four cross coats
Visual evaluation	2	2/3	3
Adhesion	2	3	4
Wet rub fastness	2	2/3	3
Dry rub fastness	2	2/3	3
Light fastness	2	2	3

4. Conclusion

It has now been possible to utilize the mixed rare earth oxides, which is obtained as a by-product after removal of radioactive thorium from monazite sands as a possible environmentally benign colorant. The process of formulating the oxide colorant (REO) for application in leather finishing has been optimized with particle size of 45 μm, the coating of the pigment particles with hydrophilic agents like PVA at a ratio of 1:0.8 to overcome the steric hindrance factors and hence better interaction between pigment and binder, a ball milling time of around 8 h. At this ratio the leather is more hydrophobic in character. The pigment was compatible with various other auxiliaries employed in leather finishing and meets the current requirements for pigments like upgrading of finished leather through excellent covering of surface and improved levelness, no overloading of grain, excellent physical properties, ageing resistance and miscibility with water.

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Table 7
Effect of nature of binder on the finish film characteristics

Parameter	Soft	Medium	Hard	Micro
Visual evaluation	3	3	3	3
Adhesion	2/3	2/3	4	2/3
Wet rub fastness	2/3	3	3	2/3
Dry rub fastness	2/3	3	3	2/3
Light fastness	2/3	2/3	3	3
Color				
L	21.3	26.0	20.6	28.7
a^*	21.0	21.3	19.0	23.6
b^*	29.9	33.4	28.2	41.9
γ_s^p (mN/m)	4.0 ± 0.2	3.3 ± 0.1	3.6 ± 0.4	5.6 ± 0.2

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