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Artists' Color

1. Introduction

The three major components of artists' colors are pigments, binders, and fillers. Pigments change appearance by selective absorption and/or scattering of light. Pigments determine the hue, hiding power, and tinting strength of artists' colors. Important pigment properties include tinting strength, light fastness, weather resistance, hiding power, transparency, shade, dispersibility, and chroma. Binders enable the pigments to adhere to the substrate. Fillers can influence optical properties such as whiteness and hiding power (e.g., synthetic silicates and blanc fixe as partial replacements for white pigments), rheological behavior, mechanical properties, and resistance to weathering and chemicals.

2. Major Components [1]

2.1 Pigment

Two kinds of pigments are generally used in making artists' color: organic pigment and inorganic pigment.

2.1.1 Organic Pigments

Table 1 lists most organic pigments for artists' colors. Organic pigments can be classified into azo pigments and polycyclic pigments.

C.I. name	C.I. number	Pigment type	Lightfastness[a]
Pigment Yellow 1	11680	monoazo	**
Pigment Yellow 3	11710	monoazo	**
Pigment Yellow 65	11740	monoazo	**
Pigment Yellow 74	11741	monoazo	**
Pigment Yellow 83	21108	disazo	**
Pigment Yellow 97	11767	monoazo	**
Pigment Yellow 108	68420	anthrapyrimidine	**
Pigment Yellow 150	12764	azo Ni-complex	***
Pigment Yellow 151	13980	benzimidazolone	***
Pigment Yellow 155		bisacetoacetarylide	***
Pigment Orange 5	12075	β-naphthol	**
Pigment Orange 34	21115	disazo	*
Pigment Orange 43	71105	perinone	***
Pigment Orange 62	11775	benzimidazolone	***
Pigment Orange 67	12915	pyrazoloquinazolone	***
Pigment Orange 73		diketopyrrolopyrrole	***
Pigment Red 9	12460	naphthol AS	**
Pigment Red 83 : 1	58000 : 1	alizarin crimson	*
Pigment Red 112	12370	naphthol AS	**
Pigment Red 122	73915	quinacridone	***
Pigment Red 144	20735	disazo condensation	**
Pigment Red 170	12475	naphthol AS	**
Pigment Red 176	12515	benzimidazolone	**
Pigment Red 179	71130	perylene	***
Pigment Red 188	12467	naphthol AS	**
Pigment Red 202		quinacridone	**
Pigment Red 253	12375	naphthol AS	**
Pigment Red 254	56110	diketopyrrolopyrrole	***
Pigment Brown 25	12510	benzimidazolone	***
Pigment Brown 41		disazo condensation	***
Pigment Violet 19	73900	quinacridone	***
Pigment Violet 23	51319	dioxazine	***
Pigment Violet 29	71129	perylene	**
Pigment Blue 15 : 3	74160	copper phthalocyanine	***
Pigment Blue 16	74100	phthalocyanine	***
Pigment Blue 60	69800	indanthrone	***
Pigment Green 7	74260	copper phthalocyanine	***
Pigment Green 36	74265	copper phthalocyanine	***

Table 1. *Organic pigments used for artists' colors (CI: color index, * represents the lightfastness scale -- the more *, the higher lightfastness)*

Azo Pigments mainly cover the range of yellow, orange, red, violet, and brown shades. Examples for monoazo pigments are C.I. Pigment Yellow 1, Pigment Orange 5, Pigment Red 112, Pigment Red 176, and disazo pigments include C.I. Pigment Yellow 83, Pigment Orange 34, and Pigment Red 144 (Table 1).

Polycyclic pigments include:

- Phthalocyanine pigments (e.g., Pigment Blue 15:3, Pigment Green 36)
- Quinacridone pigments (e.g., Pigment Red 122, Pigment Violet 19)
- Perylene and perinone pigments (e.g., Pigment Violet 29, Pigment Orange 43)
- Isoindolinone and isoindoline pigments (e.g., Pigment Yellow 110)
- Anthrapyrimidine pigments (e.g., Pigment Yellow 108)
- Diketopyrrolopyrrole pigments (e.g., Pigment Red 254)

2.1.2 Inorganic Pigments

All inorganic pigments contain heavy metal constituents with the exception of titanium dioxide, carbon black, and ultramarine pigments (Table 2).

C.I. name	C.I. number	Common name	Composition
Pigment White 1	77597	lead white	$2PbCO_3 \cdot Pb(OH)_2$
Pigment White 4	77947	zinc white	ZnO
Pigment White 6	77811	rutile	TiO_2
Pigment White 18	77220	chalk	$CaCO_3$
Pigment White 19	77002	clay	$Al_2O_3 \cdot SiO_2$
Pigment White 22	77120	blanc fixe	$BaSO_4$
Pigment White 24	77002	alumina hydrate	$Al(OH)_3$
Pigment Yellow 35	77205	cadmium zinc sulfide	$(Cd,Zn)S$
Pigment Yellow 42	77492	synthetic hydrated iron oxide	$FeOOH$
Pigment Yellow 53	77788	nickel antimony titanium yellow (rutile)	$(Ti,Ni,Sb)O_2$
Pigment Yellow 184	-	bismuth vanadate/molybdate	$4BiVO_4 \cdot 3Bi_2MoO_6$
Pigment Orange 20	77202	cadmium sulfide/selenide	$Cd(S,Se)$
Pigment Red 101	77491	synthetic oxide	Fe_2O_3
Pigment Red 108	77202	cadmium sulfide/selenide	$Cd(S,Se)$
Pigment Brown 7	77491	sienna/umber	Fe_2O_3
Pigment Brown 24	77310	chromium antimony titanium (rutile)	$(Ti,Cr,Sb)O_2$
Pigment Brown 33	77503	zinc iron chromite brown (spinel)	$(Zn,Fe)(Fe,Cr)_2O_4$
Pigment Violet 14	77360	cobalt violet phosphate	$CO_3(PO_4)_2$
Pigment Violet 15	77007	ultramarine red/violet	Na,Si,Al,S
Pigment Violet 16	77742	manganese violet	$(NH_4)Mn(P_2O_7)$
Pigment Blue 27	77510	Prussian blue	$NH_4[Fe(II)Fe(III)(CN)_6] \cdot H_2O$
Pigment Blue 28	77346	cobalt blue (spinel)	$CoAl_2O_4$
Pigment Blue 29	77007	ultramarine blue	Na,Si,Al,S
Pigment Blue 33	77112	manganese blue	$BaMnO_4/BaSO_4$
Pigment Blue 35	77368	cerulean blue	Co_2SnO_4
Pigment Blue 36	77343	cobalt chromite blue (spinel)	$Co(Al,Cr)_2O_4$
Pigment Green 17	77288	chrome oxide green	Cr_2O_3
Pigment Green 18	77289	viridian	$Cr_2O_3 \cdot 2H_2O$
Pigment Green 19	77335	cobalt nickel zinc titanite green	$(Co,Ni,Zn)_2TiO_4$
Pigment Green 23	77009	green earth	iron(II) silicate with clay
Pigment Green 26	77344	cobalt chromite green (spinel)	$CoCr_2O_4$
Pigment Green 50	77377	cobalt titanate green (spinel)	Co_2TiO_4
Pigment Black 7	77266	carbon black	almost pure C
Pigment Black 9	77267	bone black	$Ca_3(PO_4)_2/C$
Pigment Black 11	77499	black iron oxide	Fe_3O_4

Table 2. *Inorganic pigments for artists' colors*

2.1.2.1 White Inorganic Pigments

The largest group of the inorganic pigments is the white pigments, and they are among the most important in the artists' palette. The four major white pigments in use today are titanium dioxide (TiO_2, C.I. Pigment White 6), zinc white (ZnO, C.I. Pigment White 4), blanc fixe ($BaSO_4$, C.I. Pigment White 22), and white lead [$Pb(OH)_2$ .2 $PbCO_3$, C.I. Pigment White 1]. Nowadays, especially because of the toxicity, the use of lead white is limited to restoration only.

Titanium dioxide (C.I. Pigment White 6) is of outstanding importance as a white pigment because of its scattering properties, its chemical stability, its biological inertness, and its lack of toxicity. In order to improve its weather resistance, lightfastness, and dispersibility, this pigment is frequently coated with colorless organic or inorganic compounds of low solubility.

Zinc white is a fine white powder, which is amphoteric; it reacts with organic and inorganic acids, and it also dissolves in alkalis to form zincates.

Barium sulfate (blanc fixe) is of lower hiding power than white lead, but has resistance to hydrogen sulfide. In artists' colors, barium sulfate is often used to adjust the consistency of the liquid paint.

2.1.2.2 Colored Inorganic Pigments
The colored inorganic pigments can be from the natural earth or synthetic one.

Natural Earth Pigments
Today, natural earth pigments used as artists' pigments are green earth (ferrous silicate with clay, C.I. Pigment Green 23) and natural iron oxides. Of the natural iron oxide pigments, hematite (α-Fe_2O_3) attained economic importance as a red pigment, goethite (α-FeOOH) as a yellow pigment (C.I. Pigment Yellow 43), and the umbers and siennas as brown pigments (C.I. Pigment Brown 7). The natural earth pigment has poor tinting strength and less saturated color shade due to their low purity and broader particle size distributions. However, synthetic pigments could overcome the weakness of natural earth pigments. Clays or silica are frequently present in natural earth pigments.

Synthetic iron pigments include α-FeOOH (iron oxide yellow, C.I. Pigment Yellow 42), α-Fe_2O_3 (iron oxide red, C.I. Pigment Red 101), and Fe_3O_4 (iron oxide black, C.I. Pigment Black 11). Synthetic iron oxides are produced under controlled conditions by a number of manufacturing processes. They are chemically purer and, because of their higher iron content, exhibit greater brightness than naturally occurring oxides. Depending on their crystalline structure and other physical parameters, iron oxide pigments range in color from various shades of red through ocher to black.

Chromium (III) oxide, which forms the basis of chromium oxide pigments, crystallizes in a corundum lattice. Chromium oxide green pigments (Cr_2O_3, C.I. Pigment Green 17) contain only trivalent chrome. Chromium oxide pigments yield a fairly dark olive-green shade. They are largely inert chemically and therefore possess good resistance properties.

Complex Inorganic Color (CIC) Pigments
The term ''complex inorganic color pigment'' refers to the fact that such pigments are a homogenous chemical phase and replaces the formerly used term ''mixed-phase metal oxide pigment,'' which gave the false impression that they are mixtures.

Nickel antimony titanium yellow $(Ti,Ni,Sb)O_2$ (C.I. Pigment Yellow 53) and chromium antimony titanium yellow $(Ti,Cr,Sb)O_2$ (C.I. Pigment Brown 24) are rutile pigments. The rutile lattice of titanium dioxide absorbs nickel oxide or chromium (III) oxide as coloring components and antimony (V) oxide to maintain an average cation valency of four.

The cobalt blue pigments are pigments with a spinel structure obtained by partial or complete replacement of metal ions of the $MgAl_2O_4$ spinel by cobalt and chromium (e.g., $CoAl_2O_4$, C.I. Pigment Blue 28). Incorporation of cobalt and nickel in the inverse titanium spinels MgO_2TiO_4 and Zn_2TiO_4 produces cobalt green pigments (e.g., Co_2TiO_4, C.I. Pigment Green 50).

All these pigments are chemically and thermally very stable and have outstanding light fastness as well as resistance to temperature, chemicals, and weathering.

Cadmium Pigments. All cadmium pigments are based on cadmium sulfide (CdS, C.I. Pigment Yellow 37) and exist in a highly stable hexagonal crystal form. Inclusion of zinc yields greenish yellow pigments [(Cd, Zn)S, C.I. Pigment Yellow 35], and the inclusion of selenium changes the shades to orange [Cd(S, Se), C.I. Pigment Orange 20], red [Cd(S, Se), C.I. Pigment Red 108] and bordeaux. The terms "cadmium yellow" and "cadmium red" have become synonymous with brilliant yellow and red shades. Especially because of their excellent light fastness, cadmium pigments are appreciated as artists' colors.

Ultramarine Pigments. Ultramarine blue is the synthetic equivalent of the naturally-occurring semi-precious stone lapis lazuli. The unique blue color is due to polysulfides within a sodium aluminum lattice, Na6Al6Si6O24(NaSn) (n ¼ 2 – 4).Violet (C.I. PigmentViolet 15) and pink (C.I. Pigment Red 259) ultramarines are derived from ultramarine blue (C.I. Pigment Blue 29) by further oxidation and ion exchange and have a very similar structure. Ultramarines have excellent light fastness and heat stability and, apart from their sensitivity to acid, good chemical resistance.

Manganese Violet Pigments. Manganese violet pigments are manganese ammonium pyrophosphates, and are red-shade, bright, clean violets (NH4MnP2O7, C.I. Pigment Violet 16). Manganese violets have excellent light fastness, good heat stability and, apart from their sensitivity to alkalis, good chemical resistance. The excellent light fastness and purity of shade, both in mass tone and pale shades, makes
manganese violet ideal for use in artists' colors.

Iron Blue Pigments. The term "iron blue pigment" (C.I. Pigment Blue 27) has largely replaced a great number of older names (e.g., "Prussian blue," "Berlin blue," "Milori blue"). These names usually denoted insoluble pigments based on microcrystalline Fe(II)/Fe(III) cyano complexes with the formula MIFeIIFeIII(CN)6.H2O,
where MI is potassium, ammonium, or sodium, of which potassium is preferred because it produces excellent hues.

2.1.2.3. Black Pigments

Carbon black pigments (C.I. Pigment Blacks 6 and 7) are produced by thermal-oxidative dissociation of aromatic oils, e.g., by the lamp black, furnace black, and gas black processes. A further black pigment used as an artists' color is bone black (C.I. Pigment Black 9), which essentially consists of carbon (10 – 20 %) and Ca3(PO4)2 (70 – 80 %) [2].

2.2 Fillers

Fillers are used to modify or influence certain physical properties of paints. Organic pigments with high tinting strength often need a filler to adjust the consistency, hue, and hiding power. Fillers of importance for artists' colors are natural barium sulfate (baryte), precipitated barium sulfate (blanc fixe), aluminum hydroxide, calcite, precipitated calcium carbonate, and clays.

2.3 Binders

For use as paint or artists' colors, pigments must be incorporated into a liquid or paste-like phase which allows them to adhere to a surface. The general binders are listed in Table 3. Besides modern synthetic binders, natural binders are used for artists' colors. The thinning power and the rheological characteristics of the paint are important for certain techniques like impasto or thin layer, and they depend on the type of vehicle. Binders which are transparent and colorless and impart high fastness to all physical properties are preferred for artists' colors.

The binder incorporates the pigments and determines the physical and optical properties of the generated film. Physical properties are film strength, elasticity, gloss, adhesion to the ground, as well as resistance to light, weather, alkali, acid, and heat. Optical characteristics are transparency, hue, and refractive index, which determine the opacity of the pigment.

Paint generally consists of three components:

1. The film-former, a chemical that dries by polymerization, physically by evaporation of solvents, or by oxidation in air;
2. The solvent in which all other materials are dissolved or suspended if the binder is not liquid;
3. Small quantities of additives that perform special functions, such as accelerating or hindering functions, optimizing drying processes, optimizing rheology and surface properties, and controlling the open time. Combinations of film-formers are also used.

For example, the type binder for tempera paints is a combination of oil and water-soluble gum arabic (or casein) emulsified with the aid of an emulsifying agent.

Type of binder	Film former	Solvent	Thinner	Process
Natural wax	beeswax	none		physically
		turpentine	turpentine	evaporation
		white spirit	white spirit	evaporation
Natural drying oil	linseed, sunflower, safflor oil	oil	oil of turpentine, white spirit	chemical reaction with oxygen
Natural resin	dammar, mastic	oil of turpentine, white spirit	oil of turpentine, white spirit	evaporation
	shellac	ethanol	ethanol	evaporation
Synthetic resin	alkyd resins	oil of turpentine, white spirit	oil of turpentine, white spirit	chemical reaction with oxygen
	polymer dispersion	water	water	polymerization
Natural glue	animal-bone, skin, and casein glue	water	water	evaporation
	plant gum arabic and starch glue	water	water	evaporation
Synthetic glue	cellulose ether, carboxymethyl cellulose	water	water	evaporation
Natural mineral	lime, gypsum	water	water	chemical reaction with carbon dioxide (or physically with water); no film is formed
Synthetic mineral	water glass	water	water	chemical reaction with carbon dioxide to give silica; no film is formed

Table 3. *Binder for artist's colors*

3. Quality Factors

The quality of artists' colors and the final fastness of the painting are determined jointly by the binders and pigments. Pigments differ in their physicochemical and in their optical characteristics. Physically, pigments must withstand light, weather, and heat. Chemically, they must resist the action of alkali and acids. To prevent migration, the pigments must be resistant to the binder; this mainly means that they must be insoluble in the binder.

Optical properties of pigments are shade, tinting strength, light fastness, and hiding power.

Pigments can fade or darken, mainly under the action of UV radiation, which can break certain chemical bonds or change the molecular constitution. A change in chemical structure means a change of absorption in the visible region of the spectrum and a subsequent loss of tint or change of hue.

However, if the pigment absorbs UV light without any change of molecule structure, decomposition of the binder may be prevented [3].

The light-scattering power of a pigment depends on its particle size and its refractive index relative to that of the medium in which it is dispersed.

4. The Color Paint Process

The relationship between pigment and oil is critical. Oil must be available enough within the paint to properly coat and bind the pigment particles. Too much oil will lead to low color strength, excessive yellowing, and livering of the paint film. For every one percent of pigment that is added to the formula, it is considerably much harder to fully disperse as there is less oil to coat it.

In artists' paint, the size of the particle is very important; it determines the amount of light that is reflected; therefore, it also determines the color intensity of the paint. Ideally, the pigment crystalline structure should not be fractured or the color will be dull. Particle size should be less than 70 micron. The optimal particle size is 36 nm [4].

The pigment is first dispersed with the oil into a stable paste, known as the "millbase." The material is mixed in planetary or high-speed mixers for extended times to ensure the pigments are well coated in the oil. The millbase is then left to rest for a period of time to allow for the incorporation of more pigment often not attainable in the initial dispersing process. The millbase is then passed through the three-roll mill.

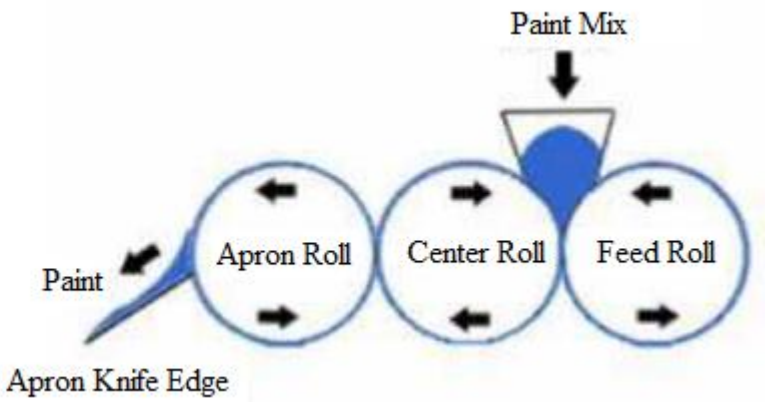

Figure 1. *The schematic drawing of three-roll mill*

The paint mixture is loaded between the feed roll and the center roll. Due to the narrowing space between the rolls, most of the mixture is rejected to the feed region. The part that does make it through experiences a very high shear force and disperses the pigment particles in the binder. As it comes out the other side, the material that remains on the center roll moves through to nip between the center roll and apron roll, experiencing an even higher shear force due to the higher speeds. The paint maker then scrapes the processed mixture off the apron roll with a knife and transfers it back to the apron. The milling cycle is repeated many times until the pigment is perfectly dispersed and the particle size is in the good range.

This graphic (Fig. 2) shows how the pigment aggregates goes into the 3-roll mill, where the pigment particles are dispersed and evenly coated by the binder, resulting in the smooth paint that is put into the tube. If the paints are not finely ground, you will see hot or shiny spots as well as cold or dull spots.

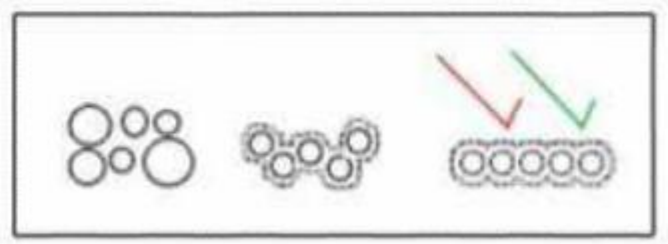

Figure 2. *A schematic drawing of the uniform distributed pigment particles*

Conclusion

High quality artists' color paint requires the fullest chromatic strength, intense tinting power, excellent lightfastness qualities, and extremely clean color-mixing potential on the palette. In order to reach the unique paint quality, the pigment dispersion and narrow distributed particle size are demanded. Three-roll mill machine plays an important role in the color paint process to achieve the high quality color paint.

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