THEMATIC UNIT Nº 6

PIGMENTS AND FILLERS.

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6.1. PIGMENTS: DEFINITION AND FUNCTIONS.

A pigment is a material that changes the color of reflected light as a result of selective color absorption. This physical process differs from fluorescence, phosphorescence, and other forms of luminescence, in which the material itself emits light. Many materials selectively absorb certain wavelengths of light, depending on their wavelength. Materials that humans have chosen and produced for use as pigments usually have special properties that make them ideal for coloring other materials. A pigment must have a high strength dyer on coloring the materials. It must also be stable in solid form at room temperature.

The pigments are used for coloring paint, ink, plastics, textiles, cosmetics, food and other products. Most pigments used in manufacturing and in the visual arts are dry colorants, usually in the form of fine powder. This powder is added to a vehicle or matrix, a relatively neutral or colorless material that acts as an adhesive. For industrial applications, as well as arts, permanence and stability are desirable properties. The pigments that are not permanent are called fugitive. Fugitive pigments fade over time or with exposure to light, while others end up black.

The pigments must not contain fillers but certain colors, because of its composition and lack of body require fillers to fix the color. In most cases, when a pigment incorporates a filler it is because they have been adulterated.

6.2. A BRIEF HISTORICAL VIEW.

The naturally produced pigments such as ochres and iron óxiodos have been used as colorants since prehistoric times. Archaeologists have found evidence that early humans used paint for aesthetic purposes, such as body decoration. There have been found pigments and tools related to that aesthetic activity that are believed to have between 350,000 and 400,000 years ago in a cave at Twin Rivers, near Lusaka, Zambia.

Before the Industrial Revolution, the variety of colors available for art and other decorative uses was technically limited. Most of the pigments used were ground and mineral pigments, or of biological origin. They were also collected and traded from unusual sources such as botanicals substances, animal waste, insects and mollusks. Some colors were difficult or impossible to prepare with the pigments available. The blue and purple were associated with royalty because of its high cost.

Biological pigments were often difficult to acquire, and production details were kept secret by manufacturers. The Tyrian purple is a pigment produced from the mucosa of one of the many species of snails of the genus Murex. Production of Tyrian purple to be used as a dye started since at least the year 1200 B.C. with the Phoenicians, and was continued by the Greeks and Romans until 1453, year of the fall of Constantinople. The pigment was expensive and difficult to produce, and objects stained with it were synonymous with power and wealth. The Greek historian Theopompus, who lived in the sixth century BC. said "purple dye was worth its weight in silver". The only way to achieve a strong and bright blue was using a semi-precious stone, lapis lazuli, which produced a pigment known as ultramarine blue. However, the best sources of lapis lazuli, were remote. The Flemish painter Van Eyck Jack (S. XV) generally did not use blue in their works. Commission a portrait in wich to be used ultramarine blue was considered a great luxury. If a customer wanted blue, he had to pay extra. When Van Eyck used lapis lazuli, never mixed with other colors, but applied it in its pure form, almost like a decorative glaze. Prohibitive price of lapis lazuli forced artists to seek alternative, less expensive pigments, both mineral (azurite) and biological (indigo).

The conquest of America by Spain in the S. XVI introduced new pigments and colors in the cultures of the peoples on both sides of the Atlantic. Carmine, a dye and pigment derived from a parasitic insect that can be found in Central and South America, attained great value in Europe. Produced from dried and crushed cochineal, carmine dyes could be used in factory, body paint or solid form, in almost any type of paint or cosmetic.

The son of a dyer, Tintoretto used Carmine red pigment derived from cochineal, to produce dramatic color effects.

The natives of Peru had produced textile dyes from cochineal since at least the year 700, but the Europeans had never seen the color. When the Spanish invaded the Aztec empire in what is now Mexico, they quickly exploited the color to have new business opportunities. Carmine became the second most valuable export of the region after silver. The pigments produced from the cochineal insect gave the Catholic cardinals their characteristic intense color clothing and the British redcoats their distinctive uniforms. The true source of the pigment, an insect, was kept secret until XVIII Century, when biologists discovered.

While Carmine was popular in Europe, blue remained an exclusive color, associated with wealth and prestige. The painter of XVIII century Johannes Vermeer often performed a luxurious use of lapis lazuli, with Carmine and Indian yellow, in his colorful paintings.

Historically and culturally, many famous natural pigments have been replaced by synthetic pigments, but have retained their historic names. In some cases the original name has changed its meaning, when applied an historic name to a popular modern color.

6.3. PIGMENTS' CLASIFICATION.

The pigments can be generally categorized into two types:

NATURAL PIGMENTS (ORGANIC AND INORGANIC TYPE).

SINTHETIC OR CHEMICAL PIGMENTS.

Obtained for lower costs of certain natural pigments. Its origin can be both organic and inorganic, but in the end are always treated chemically. Today, many of them are made from petroleum and carbon.

<u>THE ORGANIC PIGMENTS (from animals).</u>

The organic pigments are those from a matter wich was alive, that is, animal or plant origin, can be extracted from plants, leaves, wood, etc.., Or organs or animal material as the bladder, blood, etc. Its technical characteristics can be summarized as:

- They are usually quite transparent but very tinting.
- There are ones that have good lightfastness, such as ivory black (obtained from the calcination of ivory), although the majority of animal organic pigments are generally unstable to light.
- They are generally insoluble in water and costs to dilute in it.
- Regardless their toxicity or not, we pay special attention to take into account of possible allergic reactions to components thereof.

In addition to the ivory black, organic pigments have other animal origin as:

The *bone* black, obtained by calcining various bones of animals.

Cochineal carmine, obtained from the female cochineal.

Sepia, achieved from sepia ink.

Purple, which was formerly obtained from the secretion of several species of gastropod molluscs.

Indian Yellow, obtained from the urine of cows fed on mango leaves.

THE ORGANIC PIGMENTS (from plants).

As the organic pigments of plant origin can speak of characteristics similar to organic pigments of animal origin ones, so its use is not advisable given the lack of general stability.

Traditionally the plant pigments that have been most used are:

Black of vine tree or branches, obtained from the calcination of branches of the vine.

Black of peach bones and other fruit trees, obtained from the calcination of bones of different fruit trees.

Natural indigo, it's more of a dye obtained from plants of the genus Indigofera. Like all soluble dyes and need a mordant product to set. Today has been replaced by azo blue.

Garanza's Lacquer, dye obtained from the root of a plant family Rubiaceae. Called also blonde's lacquer. Today has been replaced by azo red.

Drago's Blood. Is obtained from the substance secreted as a resin or sap from a tree that grows in the Canary Islands named Drago.

Saffron, obtained from the saffron flower.

Also different dyes can be extracted by maceration, usually with alcohol, or by pressing, different flowers or plants, like lilies, geraniums, beets, carrots, etc.

Of all the colors of plant origin, the most stable are the blacks.

Today, almost all colors of animal and plant have been replaced by synthetic colors that offer better properties and are more stable.

INORGANIC PIGMENTS (mineral origin)

The mineral pigments are just that mineral origin, like iron, cupper, titanium, etc. And their technical characteristics can be summarized as follows:

- They are generally opaque, high-power coloration.
- In most cases are solid at light.
- They are dense and often are micronised to increase the ease of dispersion in the binder.

- They left "wet" well by water.
- Some, due to metal content in their chemical composition, are toxic.

The natural earth dyes are inorganic pigments that show no inconvenient for use in all kinds of paintings and lack of toxicity. Synthetic oxides from iron in its different varieties are a perfected copy of natural earths.

The first known pigments were natural minerals. Iron oxides produce a wide variety of colors and can be found in many cave paintings of the Paleolithic and Neolithic. Two examples are the red ocher (Fe2O3) and yellow ocher (Fe2O3H2O) The charcoal or black carbon, has also been used as black pigment since Prehistory.

SYNTHETIC PIGMENTS

Two of the first synthetic pigments were white lead (lead carbonate (PbCO3) 2Pb (OH) 2) and blue frit (Egyptian blue). The lead white is produced by combining lead and vinegar (acetic acid, CH3COOH) in the presence of carbon dioxide (CO2). The blue firt is copper and calcium silicate was made from colored glass with a copper mineral, such as malachite. These pigments were used since at least the II millennium b. c. Scientific and industrial revolutions led to an expansion in the range of synthetic pigments, which are manufactured or refined from natural substances, available for both commercial and for artistic expression.

Titian used the historic pigment Vermilion to produce red tones in the Fresco *Assumption of Mary*, completed in 1518.

Due to the cost of lapis lazuli, there were many attempts to find a less expensive blue pigment. Prussian blue was the first modern synthetic pigment, discovered by accident in 1704. In the early XIX century, existing varieties of blue were added synthetic and metallic blue pigments, including French ultramarine, a synthetic form of lapis lazuli, and various forms of cobalt and cerulean blue. In the early XX century, with organic chemistry added Phthalo Blue, a synthetic organic pigment enormous power stainer.

Scientific discoveries in terms of colors created new industries and produced changes in fashion and taste. The discovery in 1856 of Perkins mauve, the first aniline dye, laid the foundation for the development of hundreds of synthetic dyes and pigments. This dye was discovered by a chemist 18 years old named William Perkin, who exploited his discovery in the industry and became wealthy. His success attracted a generation of fans, as young scientists entered the field of organic chemistry for similar achievements. In the last decades of the nineteenth century, textiles, paintings and other items in colors like red, crimson, blue and purple had become affordable.

The development of chemical dyes and pigments helped bring industrial prosperity to Germany and other northern European countries, but caused dissolution and decline elsewhere. In the former Spanish empire in the New World, the production of cochineal colors employed thousands of underpaid workers. The Spanish monopoly in this production was worth a fortune to the early nineteenth century, when the War of Independence from Mexico and other changes in trade halted production. Organic chemistry gave the final hit to the cochineal industry. When chemists created a cheap substitute for carmine.

OTHER WHITE PIGMENTS

When preparing paints with organic or inorganic pigments it is recommended to add a white pigment for enhance stabilization of the painting. Remember, the "cold" pigments (light tones) is normal darken as it dries. Within the white pigments are the most common:

TITANIUM WHITE.

It has great covering power. Use it in small as proportions but the colors "get pastel appearence."

WHITE ZINC OXIDE.

Only oil paintings.

LITHOPONE.

It has good hiding power but less than white titanium. It can even be used in the manufacture of paints to 50% compared with the pigment. In exterior paints over time " becomes yellow".

SOLID WHITE.

Very little covering power. Used primarily as a load to bring down the paintings’ prices.

TALC AND KAOLIN.

They are used sometimes for give more "brushability" to the paintings.

6.4. ITS USE AND HANDLING.

The pigments have been used since prehistoric times, and have been fundamental in the visual arts throughout history. The main natural pigments used are mineral or biological origin. The need for getting less expensive pigments given the scarcity of some colors, like blue, led to the emergence of synthetic pigments.

Everything is outlined below refers only products from a general point of view. This is why it is advisable to compare these guidelines with the help of painting procedure manuals specific to each manufacturer.

As previous thing before you start working with pigments and binders is useful provided the following:

- Plastic cans of the same diameter of the mouth and base (for able to work easily)
- Spatula or glass rod to allow removal properly.
- Anatomic gloves to avoid contact our hands with the products we use.
- Surgical type mask to avoid inhaling those pigments of high volatility when breathing or oral ingestion.
- Plastic lenses to avoid possible contact with the eyes.

6.4.1. HOW TO WORK WITH TOXIC PIGMENTS?

It is important to note that many of the pigments used for artistic purposes are toxic, primarily those containing salts of lead or manganese, copper, sulfur, arsenic, etc.. For that reason, it is desirable to know the measures to be taken to avoid accidents or can contribute, because of a misuse, to the pollution of our environment. Normally the bags containing the pigments have a label indicating whether it is organic or inorganic chemical family and if it is toxic. Pigment, as in other products such as insecticides, paints, solvents, glues and so on. Must read the instructions carefully as standard labeling prior to their use.

Toxic pigments always should be used with caution putting on gloves, mask and goggles to avoid risks associated with contact, inhalation and ingestion. In If you have skin contact is recommended wash affected area with clean water at least 15 minutes, in cases of ingestion or inhalation you should attend to a clinic with emergency.

6.4.2. HOW TO WORK WITH NON TOXIC PIGMENTS?

We suggest that handled using gloves and avoid as much as possible of dust that could reach our eyes, as though it did not represent a direct risk is always a good rule to proceed with maximum hygiene.

6.5. DIFFERENCES BETWEN A PIGMENT AND A DYE.

The organic pigments when pouring on water tend to float because of its low density, although as explain later can be diluted to form a pulp. Direct fire burned pass directly black color to become carbon. Typically the dyes are known generically, and improper, anilines. The "anilines" are soluble in water and not suitable for preparing paints. Usually a distinction is made between a pigment, which is insoluble in the vehicle (forming a suspension), and a dye, which is either a liquid or soluble in the vehicle (resulting in a solution). A dye may be a pigment or a dye depending on the vehicle in which it is used. In some cases, a pigment can be manufactured from a dye by precipitating a soluble dye with a metal salt.

6.6. PREPARATION OF PIGMENTS FOR WATER PROCEDURES.

The pigment powder is a solid and binder is a liquid or a paste (water, resins, etc.) so it is necessary that the solid becomes too a pasty mass.

- Determine the amount of pigment to use (Ideally by weighing) and if this is not possible by level tablespoons, volume ... and pour into the pot that we use to prepare mass.

- Add one tablespoon of water (ideally use distilled water) and is stirring with the spatula or glass rod. If the pigment is organic we must insist on stirring until to form a mud. If when removing still floats some pigment on the sides, add more water until lump-free paste and honey-like appearance.

- If you want to refine the mass you can incorporate a few drops of a "wetting for water-based paint, "which acts as a dispersant. Do not put too much because it is a fatty alcohol that may slow drying paint.

- If there was foam, let it rest and if will disappear. The pulp resultant may be stored in tightly closed pot with a millimeter layer of water to prevent drying.

6.7. PIGMENTS SUITABLE FOR VINYL OR ACRYLIC TEMPERA.

In general they are the most recent appeared. Are therefore of synthetic.

CADMIUM RED

QUINACRIDONE RED

NAPHTHOL CRIMSON

IRON OXIDE RED

AZO YELLOW

CADMIUM YELLOW

YELLOW OCHRE

NATURAL SIENNA

BURNT SIENNA

NATURAL UMBER

BURNT UMBER

PHTHALOCYANINE BLUE

ULTRAMARINE BLUE

PURPLE DIOXACINA

PHTHALOCYANINE GREEN

CHROMIUM OXIDE GREEN

TITANIUM WHITE

BLACK IVORY.

The essential are underlined.

6.8. PIGMENTS SUITABLE FOR WATERCOLOR.

They are generally synthetic organic pigments. The pigment, in the watercolor proceduremust be very finely ground and thin, with little body to avoid covering too much and so facilitates its penetration into the paper fiber wich is going to be used as a support.

NATURAL UMBER

BURNT UMBER

BURNT SIENNA

NATURAL SIENNA

INDIAN RED

LIGHT RED

YELLOW OCHRE

ALIZARIN RED

QINACRIDONA (PINK)

CADMIUM RED

AUREOLÍN
AZO YELLOW (FROM ARILAMIDA)

CADMIUM YELLOW

ULTRAMARINE BLUE

COBALT BLUE

MANGANESE BLUE

CERULEAN BLUE

PHTHALOCYANINE BLUE

PHTHALOCYANINE GREEN

VIRIDIAN
GREEN EARTH

CHROMIUM OXIDE

DAVY GRAY

CHARCOAL GREY

IVORY BLACK

6.10. SCHEME WITH RELEVANT CUALITIES OF PIGMENTS.

Pigments	**Téchniques**	**Origin**	**Stability**	**Qualities**
Titanium White	All	1840	Lots	+ Warm
Zinc White	All	1920	many	Cold Tonality
Lithopone White	Temperas and industrial painting	1874	medium	
Ivory Black	All	ancient	Many	Warm Tonality
Black Vine	All Suitable for Fresco	Prehistory	Many	
Black Smoke	No is well hydrated, just add alcohol.	Roma	Many	
Black Earth (Black Mineral)	All	Prehistory		Is not very intense
Naples Yellow	All	1750 Vesuvius	Many	It is used as a substitute for white to clear
Cadmium Yellow (light, medium and dark)	Doubtful at Fresco	1846	Dark Good Light Medium	
Yellow Ochre	All	Prehistory	Many	
Red earth (Ocher) and ocher Fresh	All specially Fresco	Prehistory	Many	
Cadmium Red	All but Fresco	1925	Many	

Cobalt Blue	All	1828	Good	
Manganese blue or turquoise	All	1935	Good	
Transparent Chrome Green and emerald	All	1838	Many	Toxic
Chrome green opaque	All for Fresco	1862	Many	Non-Toxic
Manganese Violet	Oil and Tempera. Not for Fresco or Watercolour	1868	Good	
Natural Umber or Burnt Umber	Fresco Tempera Oil goes dark	Antiquity	Many	Non-toxic
Brown from mars	All	1850	Many	Non-Toxic

TABLE OF PIGMENTS BOUND TO ITS CHEMICAL COMPOSITION

Pigments	**Composition**	**Noxiousness**	**Stability**	**Comments**
White Plumb	Basic Plumb Carbonate	Poisonous	Low	Do not mix with colors containing cadmium. Excellent to clarify
Titanium White	Titanium Dioxide		Very High	No mixing with colors containing cadmium. Opaque, bright, intense
Zinc White	Zinc Oxide		Very High	When mixed, tends to greyish. Low covering power,

				strong, used for glazing.
Cerulean Blue Imitation	Barite Sulfate and Phthalocyanine Blue		Very High	High Dying Power
Cerulean Blue Genuine	Cobalt Stannate		Very High	Opaque Unchangeble mixing with other colors.
Cobalt Blue	Cobalt Aluminate		Very High	Excellent resistance to light. Stable when mixed with other colors.
Blue Prusia -	Iron Ferrocianuro		High	Do not use alcohol to moisten.High coloring power. Very drying action on the egg
Ultramarine Blue	Sodium sulphide and alumina-silica		Very High	Intense. Do not mix with chrome yellow
Naples Yellow			Many	It is used as a substitute for white to clear
Cadmium Yellow (light, medium and dark)			Dark Good Light Medium	Doubtful at Fresco
Yellow Ochre			Many	Suitable for all procedures

Red earth (Ocher) and Toasted Ocher			Many	Suitable for all procedures Specially for Fresco
Cadmium Red			Many	Suitable for all procedures but Fresco
Cobalt Blue			Good	Suitable for all procedures
Manganeso Blue or Turquose	Manganato	Poisonous	High	
Transparent Chrome Green and emerald		Toxic	Many	Suitable for all procedures
Opaque Chrome Green		Non-Toxic	Many	Suitable for all procedures specially for Fresco
Manganese Violet			Good	Oil and Tempera. Not for Fresco or Watercolour(casein)
Natural Umber or Burnt Umber		Non-Toxic	Many	Fresco Tempera Oil goes dark
Brown from mars		Non-Toxic	Many	

6.10. FILLER MATERIAL: DEFINITION AND TYPES.

Is so called the additional materials of mineral origin, chemically inert, non hygroscopic, and with a refractive index very low, i.e. of little colorant power to be agglutinated with oils, but not with aqueous binders. These substances can not be considered properly pigments although in many cases are white, because essentially serve to give body, opacity and weight as well as to cover the pores of the support and to adulterate pigments.

As happened with the colors, the number of available fillers is very large and many of them have no practical use in the field of painting techniques and procedures. Among the most widely used fillers for the field of fine arts can provide a first classification according to their composition:

- Sulfates
- Carbonates
- Silicates
- Silica
- Others

SULPHATES

Sulfates are usually found in fields produced by volcanic activity. The sulfates most commonly used for artistic purposes are: calcium sulphate (gypsum) and barium or barite sulfate.

CARBONATES

The *natural calcium carbonate* receive the highest quality, among others, the names of *white from Spain(Pypeclay), Paris' white and browning white or plaster*. Some of its features are the large volume that contributes to the matters with which is mixed, so that makes it ideal as filler material, its ability to adulterate paints, the possibility of acting as a white pigment in procedures to water. Should also be noted that it doesn't produce toxic effects, and presents a great stability to all pigments and binders so their degree of conservation in a work of art, in normal conditions is very high.

The *Crete* is another calcium carbonate traditionally employed as filler. It has the same composition as *calcite, white of Spain(Pypeclay), and marble dust*, but no impurities and is much whiter.

The marble dust, since ancient times has been used primarily for the preparation of mortars of great whiteness and quality for fresco painting. Is obtained primarily from white marble, ground in different thicknesses and texture is glassy, compact and slightly porous. Their coloring can vary depending on the type and color of the marble employed. Non-toxic except for dust inhalation. It is now more frequent use of frame powder in the development of fillers mixed with oil colors and acrylics.

SILICATE

Within the silicates we have the *Kaolin*, this is a material that offers very good qualities for use like filler material in the different pictorial techniques fats and lean. Its main use in the pictorial field is white in the pastels.

Talc, composed of hydrous magnesium silicate, is used as white pigment for the manufacture of paint in pastels and chalks. The mixture of powder paint for easy application and prevents cracking in oil paint. Also used as a degreaser and to provide opacity to paper manufacture.

The Mica, is a derivative of various classes of clays' silicates. At present, mica is used in water paints, acrylic and vinyl fundamentally, for alerting its iridescent property.

SILICA
Silica is also called chert or flint. Its chemical composition is silicon dioxide. Within this group, as traditionally used in the field of painting techniques and procedures are the *land of Tripoli, silica sands, diatomite and quartz.*

6.11. REFERENCE PRICES OF PIGMENTS AND FILLERS (2011-12).

Prizes per 100 grams.

PIPECLAY 1.10 Euros

WHITE NIEVIN 2.50 Euros

WHITE OF TITANIUM Inorganic11, 80 Euros

ZINC OXIDE WHITE Inorganic 7.50 Euros

CLEAR BLUE Organic 6.55 Euros

OVERSEAS DARK BLUE Inorganic 11 Euros

PRUSSIAN BLUE Inorganic. High toxicity. 18.40 Euros

YELLOW GOLD Organic 7 Euros

CLEAR YELLOW Organic 7 Euros

YELLOW IRON Inorganic 7 Euros

IRON RED Inorganic 6.80 Euros

CRETE Inorganic 2.10 Euros

DAMMAR RESIN BALLS 1 kg. 15.80 Euros

STONE BOARD 100 X 70 3 Euros

STONE BOARD 50 X 70 1.55 Euros

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