

HISTORY OF PAINT

The use of paint as a protective coating has come down to us from remote antiquity. Even Noah "pitched the Ark within and without with pitch" and the mother of Moses placed him in an ark of bulrushes which she "daubed with slime and with pitch." At later periods the Jews evidently used paint on their houses, as in Jeremiah appears--"Woe unto him that sayest, 'I will build me a wide house--ceiled with cedar and painted with vermillion.'" (Even then it was bad taste to paint a house with vermillion.)

Its use for decoration and picture painting began very much earlier. Pictures of bison, wild bear, reindeer and other animals have been found in some caves in Spain. These were evidently the work of cavemen and date from the Paleolithic age, probably 50,000 years ago. These prehistoric pictures are real masterpieces and are far superior to pictures of battles and hunting scenes on the wall of Babylon erected about 2500 years B.C. and wall paintings found in tombs in Thebes dated from 1500 B.C. The picture of the bison is in reality an animated cartoon, illustrating the animal running--the legs are shown in three positions, at the beginning, middle, and end of the stride.

In the British Museum are many mummies elaborately decorated, the oldest of these is that of Mekara who lived about 4000 B.C. Many beautifully painted things were found in the tomb of King Tutankhamen where they had lain undisturbed for 3000 years. These references seem to establish the use of paint at least 4000 years before the coming of Christ.

The art of painting developed much more slowly than did sculpture. This was undoubtedly due to the crude nature of painting

materials available rather than to the skill of the artist. Greek sculpture attained a high state of development as early as four or five centuries B.C. but the art of painting was not fully developed until the remarkable works of the Italian masters in the fifteenth century. Pliny, who lived A.D. 23 to 79 and was killed when the eruption of Mount Vesuvius destroyed Pompeii, writes of painting as a waning art, but from the records there must have been some wonderful painters among the ancient Greeks.

The materials used by the ancients were largely minerals, natural earth colors, with a few organic dyes from plants and waxes. The old Greek philosophers are the first to give any definite reference to detail. Theophrastus, writing about 350 years B.C., refers to "cerussa" a native mineral carbonate of lead found in small quantities in Europe, and Pliny records the mode of boiling wax and painting ships with it after which--"ncither the sea, nor the wind, nor the sun can destroy the wood thus protected."

The Romans, being essentially a war-like people, never brought the decoration of buildings to the high plane it reached with the Greeks, though the ruins of Pompeii show many structures with mural decorations in very fair condition. The colors used are glaring, usually a black background with bright red, yellow, and blue. The black was, undoubtedly, Lamp Black; the Red was the mineral Cinnabar, natural Vermilion referred to by Theophrastus and Pliny. This has stood for these centuries with little change of color.

The yellow, no doubt, was Yellow Ochre, as pots of Yellow Ochre were found at Pompeii, and the blue, undoubtedly, was Lapis Lazuli, the true native Ultramarine Blue which is found in Persia. A remarkably permanent blue used in Egyptian tombs, erected about 3000 B.C., was recently analyzed. This was found to be very similar to present day

Ultramarine. The chemists analyzing this concluded it was an artificial pigment.

The earliest reference to the manufacture of any paint material is by Theophrastus, who described White Lead as prepared from lead and vinegar evaporated to dryness. Pliny again mentions it. It is not known when the white lead of today was first made, or to what country it owes its birth, but tradition assigns discovery of the method to the Dutch and a man named Stratingh. It must be over 300 years old, as a patent for a method like the present Old Dutch was taken out in England in 1622. The length of time involved, encouraged effort to develop a more rapid method and the first quick process on record is the Chamber process patented by Sir James Creed in England in 1749. Many other processes have been invented but the most satisfactory one now in use is the Carter process patented in July, 1889.

Zinc white seems to have been suggested first by Curtois of Dijon, France in 1782, and after several unsuccessful attempts to use it for a paint material, Leclair in 1845 found a method to use it for oil paints. Up to this time all zinc oxide was made by the French process from vapors given off by a bath of zinc metal. In 1856 Wetherill patented the American process of making zinc oxide directly from the ore, mixed with coal, by volatilization on a grate.

In 1879 the Lewis patent for making sublimed lead was taken out. A vein of lead and zinc ore was discovered in 1870 and smelting it by the Lewis method developed leaded zinc like the Ozlo pigment made by the Sherwin-Williams Company. Zinc sulphide has recently been accepted most favorably because of its intense whiteness and great opacity.

Lithopone was first patented in 1874 under the name of Orr's White. There are many variations in the manufacturing process now in use, but all produce a material essentially the same. Present methods produce a very fine intensely white pigment specially adopted to flat wall paints. There are four distinct types---barium lithopone, calcium lithopone, titanated lithopone and high strength lithopone.

The element Titanium was discovered in 1791 in England occurring in the form of a black sand. It was first called Titanic Earth, having reference to the mythological sons of the earth. From this name "Titanium" was derived. The first attempt to use titanium dioxide as a paint pigment is credited to J. W. Ryland, Birmingham, England, in 1869. However, it was not developed definitely as a white pigment until 1908 by Dr. Rossi of the Titanium Alloy Company of Niagara Falls. For a time, most of the material was made from Florida sands, but now most of the primary material comes from Illmenite developed in India. Its brilliant whiteness and great density of color made it a most acceptable pigment for paints and enamels.

Black appears to be the earliest coloring pigment used, as from time immemorial soot has been used by savage tribes to paint their faces and color other objects they wished to beautify in this way. Black substantially the same as our present Lamp Black was made by the Chinese at least 2000 years ago by burning oil in small earthenware lamps with a limited supply of air and collecting the soot thus condensed. Asphalt or Bitumen found on the shores of the Dead Sea were used by the early Egyptians on mummy cases. At a much later date, in Europe, Ivory and Bone Blacks were made by burning ivory cuttings or bones in closed retorts and grinding and refining the charred residue. Frankfort or Vine

Black was made by a similar method using vine cuttings, stones from plums, olives, almonds, or similar fruits. Carbon Black, made by the incomplete combustion of gas, was first made in this country in 1864.

The earliest blue on record is Indigo used in India and Egypt and mentioned by the ancient Byzantine writers as well as Pliny and others. It is named in the Marseilles Tariff of 1226. It is produced from the indigo plant. Natural Ultramarine Blue, Lapis Lazuli, was used many centuries ago, but ultramarine was first made artificially by Christian Gmelin in France in 1828. Prussian Blue was first made in 1710 by a color maker named Diesback in Berlin. The Sherwin-Williams Company's first connection with the industry was through Lewis Steigenger, who came to London in 1760 and started the manufacture of Prussian Blue in England. He was the founder of Lewis Berger & Sons, Ltd., our present English connection, and the formula used by us today in making Prussian Blue is modified only slightly from his method. His method illustrates a formula we have dated 1756 in which he states he started with three pounds of Ox's Blood and through a complicated procedure finally resulted in 7 ounces of fecula "whose beauty will make sufficient amends for the small quantity, as it will surpass in this respect all the blues of Prussia which are prepared by other methods."

Malachite green copper mineral was employed by the ancients. Verdigris was used by the Romans as a pigment and has been detected in the wall paint of Pompeii. Paris Green or Emerald Green was discovered in 1814, though Schoele's Green very similar to this was made in 1778. This pigment is little used as a paint material now. Chrome Greens essentially the same as those now used were first made in France in 1838.

Yellow Ochre, one of the most ancient pigments, was used by the Egyptians, Greeks, and Romans. Naples yellow, which is basic lead antimoniate, has been found on Babylonian bricks at least 2500 years old. Chrome yellow, lead chromate, in common use today, was first made about 150 years ago, though some is found in nature.

The browns, such as Umber, Sienna, Iron Oxide, etc., were natural earth colors which probably were some of the earliest pigments used for decorative purposes. In the early days the Berger Company offered Mummy Brown which was actually made from the body of a mummy ground up in poppy seed oil. Shakespeare had Othello give Desdemona a lace kerchief dyed with Mummy.

The earliest red pigment about which we have any information is the native Cinnabar, mercuric sulphide, used by the ancients and Chinese. Chinese or English vermilion is now produced artificially by combining mercury and sulphur in a process submitting it to sublimation or by a wet method. This manufacture was first undertaken in England about 150 years ago. Red pigment using organic dye derived from the madder plant, a native of Greece, was made in Europe in the 13th century, though madder was used by the Greeks and Romans for ^{dye} ~~dyeing~~ long before it was used for painting. Many other organic dyes have been used, but these have been largely displaced by aniline dyes first discovered by Dr. Wm. Henry Perkin in 1856. He made, in that year, a mauve dye used to dye silk for a dress for Queen Victoria. For this he was knighted.

In recent years a wide range of beautiful colors have been developed by chemical processes, such as chrome yellows, which are combinations of lead and chromium, prussian blue, which is a combination of potash and iron, and most important of all, a tremendous variety of

very beautiful colors covering the entire range of the rainbow produced from coal tar.

The history of paint vehicles and varnishes can be presented much more simply than that of pigments. The pitch that Noah used was, undoubtedly, a form of crude petroleum, and it is remarkable that no other substance has been discovered that is so well adapted to protect surfaces against moisture. Our present day Ebonol and other roofing materials are direct lineal descendants.

Paint is essentially a compound of drying oils and pigments (either colored or white) intended to beautify and preserve the surface to which they are applied. The oils serve as binders holding the pigment together and also binding it to the surface. The life of the paint film depends to a high degree on the oils which are used.

Waxes were first used as the vehicle for colored paints. Excellent examples of the use of melted wax as a binding medium for pigments, executed in the second and third centuries, are shown in London museums. Later, evidently, a mixture with oil or animal fat was used to lessen the inconvenience of heating the wax. For interior decoration a size made with fish glue, gum arabic, or similar gum or the white of an egg, were the earliest mediums used.

The earliest mention of drying oils as a paint vehicle is by Aetius, a Greek Physician, in the beginning of the sixth century. This may have been Linseed Oil. Heraclius, in the seventh century, first mentions the mixing of oxide of lead with oil to make it dry quicker. In the library at Lucca is a manuscript of the eighth or ninth century, giving a recipe for a transparent varnish composed of Linseed Oil and Varnish Gum, probably amber. Oil painting had been definitely established

as early as A.D. 1100, though in an unsatisfactory form. In fact, the art of painting was very crude until the fifteenth or sixteenth century when it underwent a transition from ancient to modern art. About this time, other oils such as poppy seed oil and walnut oil came to be much favored. Linseed oil is the best known and most widely used oil in the paint industry which position it has held for centuries.

China wood oil, or tung oil, though employed by the Chinese from time immemorable, in finishing their junks and for lacquers, was introduced into the manufacture of varnishes only about 50 years ago. Dependence on China as the sole source for tung oil has frequently caused great disturbances in the paint and varnish industry, and tung groves have now been established in this country with excellent success.

In recent years tung oil has met with considerable competition from dehydrated castor oils such as Sherwin-Williams Dchydrol. For certain purposes and particularly where whiteness and color retention are important, these oils are superior to tung oil.

Perilla oil was first introduced into the United States in 1910 by Dr. Fairchild, explorer of the Bureau of Plant Industry. The good drying quality made it very desirable in paint and varnish. Experimental plantings in the United States have been conducted since 1917 with encouraging results, but as yet no considerable quantity is grown here.

Soybean oil was introduced into the United States for use in paint and soap about 1908, though the soybean has been an important food product in China and Japan since ancient times. Use of this oil has recently been most vigorously advocated, but its slow soft drying quality prevents its use except with liberal proportions of other drying oils.

Fish oil obtained from the bodies of many fish, particularly the Menhaden, Pilchard, and Sardine, properly refined, is especially useful in coatings for metal surfaces subjected to heat.

The pigments, first wetted with some of the liquid, are finely ground on special paint mills. In the early days of the paint business, stone mills were used similar to those used in making flour. Later ball mills were developed. These are essentially tumbling machines with a large number of steel balls in them which break down the pigment to a very fine consistency. Still more recently roller mills were evolved. These result in a fine grinding of the pigment, providing a smooth film of paint free from coarseness and roughness.

Varnish differs from paint in that it contains with the oils, various resins, either natural or synthetic, which impart higher gloss and hardness to the film. When color is added to varnish, it becomes enamel.

Thinners such as turpentine or mineral spirits are necessary in paint, varnish or enamel to provide ease of application. Without the thinner, the product would be too viscous and could not be applied in uniform coating. The thinners play no part in the finished job because they evaporate as the paint film dries.

Turpentine from the European pine tree dates back for many centuries, but American turpentine that we know today was first developed by the early settlers in the southern states about 300 years ago. During the past 35 years, very satisfactory turpentine has been distilled from old pine tree stumps; also, sulphate wood turpentine has been recovered from pulp wood used in paper manufacture.

Naphtha and several grades of mineral spirits are, of course, developments from petroleum discovered in the United States by Colonel Drake who sunk the first oil well in Titusville, Pennsylvania in 1859.

The varnish gum first used probably was amber as it is found quite generally throughout Europe and beads made from it were found in early British graves and Etruscan tombs. Other varnish gums such as Zanzibar, the Sierra Leone, Benguela, Mastic, Sandarae, no doubt preceded the modern Kauri and later Manilla, Brazilian and Congo gums. Shellac has been known to the natives in India for several thousand years and used as a varnish gum for some centuries as a manuscript issued by Akbar, Emperor of Hindustan in 1590, mentions the proportions of shellac gum to be employed in varnish used for the woodwork of public buildings. (This seems to be the first definite reference to specifications for paint and varnish materials.)

In late years synthetic resins have largely replaced the natural resins originally used in paints and varnishes. Some natural resins such as rosin and damar came from the live tree, but most of them were fossil resins taken from trees that died years ago. The fossil resins produced a much more durable finish than was obtainable with rosin.

The supply of fossil resins was always limited and uncertain. Furthermore, they required much more drying time than is feasible under modern conditions. This is important because if the finish takes too long to dry it soon picks up a lot of lint and dust from the air. This makes an unsightly finish which has to be rubbed down at considerable expense in order to get a smooth finish.

Modern synthetic resins have overcome these difficulties. Compared with the old style of finish the new varnish and enamels dry more quickly, are more uniform and easier to control, and have maximum elasticity and life. They are members of a very large plastic family which is penetrating into so many fields. There are hundreds and hundreds of such resins covering every need in the paint and varnish industry. Bakelite and Alkyd Resins are probably the best known.

In the above we have not touched on lacquers which come into a special and separate class by themselves. Lacquers require the same pigments as described above where a colored affect is desired, but do not involve the use of oils such as are used in paints and varnishes. Lacquer is nitrocellulose dissolved in suitable solvents. Nitrocellulose is cotton, treated with nitric and sulphuric acids so that the cotton goes completely into solution. This is a finish used on most automobiles, airplanes and various other objects.

Lacquers do not depend upon the drying action of oil as described above. The solvents which are all very highly volatile quickly dissipate into the air leaving a celluloid-like film on the surface which is smooth, hard and durable. Because of its exceptionally fast drying qualities, lacquers do not lend themselves to brush application and are used for spray and dip work only, mostly spray.

Within the last two or three years there has been another great change in the paint business and that is the synthetic latex wall finishes, as represented by Sherwin-Williams' Super Kem-Tone. Here the oils are replaced by liquid synthetic latex (rubber.) This type of finish is coming into wide use because of its extraordinary toughness and washability.