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THE STORY OF PAINT AND VARNISH. PART

E. C. HOLTON, THE SHERWIN-WILLIAMS COMPANY, CLEVELAND,

Any attempt to tell the story of paint and varnish is certai back to the time antedating authentic history. Today w this industry as a branch of chemistry and recent writers expression to the thought that it is now rapidly coming un control, having been rescued from the empiricists within or three decades.

However true this may be, we moderns are too eager to ex cent meager steps forward and to belittle the tremendous adva those who preceded us and built the roads for our forward ma

Nature is and always has been the Master Artist. He of color has ever inspired man in his attempt to imitate h tutored savage in all ages and in all climes has attempted to b self and his surroundings by following in her footsteps. Ev tion, of which we have any knowledge, has made use of c and other colored minerals for decorating its people, its implements and trappings of war, the paraphernalia used in th medicine, religious rites, burial of the dead, etc.

In ancient Assyria, in ancient Egypt, and in ancient Maya, bers, copper and cobalt compounds, whiting, charcoal, and ot were used. In India, China, and Japan, pigments, paints, have long been used. In ancient Greece and in Rome oth than those found in nature had come into use. In Europ middle ages several new pigments were added and by th the last century nearly all of the mineral pigments known in use.

Pliny in his Natural Philosophy gives some idea of the sta at the beginning of the Christian Era.

He describes pigments which we recognize as lampblack, ivory black, vine black, realgar, orpiment, bole, yellow, red ochres and umbers, also blue and green copper minerals, white lead, red lead, cinnabar, white mineral substances pro nature of talc or asbestine and chalk, also a purple lake which mineral dyed with Tyrian purple and a green lake which w mineral dyed with weld. These pigments were applied as or with wax in encaustic painting.

"Purpurissum," a Tyrian purple lake, was used with glai glaze over "Sandyx" orange mineral red lead, to give the a "minum," mercury vermilion. "Purpurissum" was also use over "Caeruleum."

The following excerpts from Pliny are of interest.

BOOK XXXIII, CHAP. 27

Native chrysocolla, known as "uva," differs from the other in its hardness more particularly; and yet hard as it is it admits of being colored with the plant known as "luteum." Like flax and wool it is of a nature which imbibes liquids. For the purpose of dyeing it is first bruised in a mortar, after which it is pressed through a fine sieve. This done it is ground, and then passed through a still finer sieve; all that refuses to pass being replaced in the mortar, and subjected once more to the mill. The finest part of the powder is from time to time measured out into crucibles where it is macerated in vinegar, so that all the hard particles may be dissolved; after which it is pounded again, and then rinsed in shell shaped vessels, and left to dry. This done the chrysocolla is dyed by the agency of schist alum and the plant above mentioned and thus it is painted itself before it serves to paint.

It is of considerable importance, too, that it should be absorbent and readily take the dye; indeed if it does not speedily take the color scytanum and turbistum are added to the dye; such being the names of two drugs which compel it to absorb the coloring matter. When chrysocolla has been thus dyed, painters call it "orobitis," and distinguish two kinds of it, the cleansed orobitis which is kept for making lomentum, and the liquid,. . . . Both these kinds are prepared in Cyprus but the most esteemed is that made in Armenia; the next best being that of Macedonia. It is Spain, however, that produces the most. The great point of its excellence consists in its producing exactly the tint of corn when in a state of freshest verdure.

BOOK XXXV, CHAP. 32

WAX, too, is stained with all these coloring substances for encaustic painting, a process which does not admit of being applied to walls, but is in common use by way of ornament for ships of war, and indeed merchant ships at the present day. As we go so far as to paint these vehicles of danger no one can be surprised if we paint our funeral piles as well, or if we have our gladiators conveyed in handsome carriages to the scene of death, or at all events, of carnage.

When we only contemplate this extensive variety of colors we cannot but admire the ingenuity displayed by the men of former days.

BOOK XXXIII, CHAP. 40

One motive, however, for giving an undercoating of syricum to minimium, is the evident saving of expense that results therefrom.

(According to Aetius, syricum was made by the calcination of pure ceruse, white lead. Book XXXV, Chap. 25.)

Insects That Work for Man

The honey bee for thousands of years has provided binding material for pigments, honey for the water colors, and wax for encaustic painting.

The lac insect of India, the coccus lacca (lacca tachardia), injures and stunts or kills the shrubs and trees on which it feeds, but in so doing there is produced a composition of resin, wax, and dye which constitutes the "stic lac" of commerce. This when crushed and washed free from the wood, bark, and dye becomes "seed lac."

"Seed lac" softened by heat and drawn into sheets and broken into flakes becomes "shellac." The most common variety is called "orange" shellac; darker grades are "garnet," "ruby," etc.

Shellac may be bleached and then is known as "white s
orange and white shellac have been and still are of gre

The insects which sting the foliage of nut tress, producing have made possible our ordinary writing inks but have also of our fastest blues and violets, the oxazine colors, which, as yet found little use in paints. There is one insect, how played a distinguished and romantic rôle. The story of th be called the romance of the red, white, and blue or the s of a happy experiment.

The cochineal louse family is very large, its members dif another according to the plant furnishing nourishment an its habitat.

The cochineal of the cactus, coccus cacti, is the hero o or more properly the heroine, since it is the female of th furnishes the coloring matter used for so many years in th mine and crimson lakes. These lady insects are either naturally, while happily feeding on the cactus leaves, o swept from their banquet tables and roasted or steamed t die to dye. Their dried bodies are shipped to the dyers a The coloring matter is extracted by means of boiling wat filtered solutions of color are treated with alum and all carbonates and other chemicals, and the beautiful carmin For hundreds of years the purple, crimson, and scarlet lake colors produced in this way.

From the lowly cactus leaf to the most gaily decorate last century and even to the bishop's cap, the king's robe donna's cheeks and lips was quite a step but this is only the story.

In 1704, Diesbach, in Berlin, while experimenting in m alumina lakes, with green vitriol, used a potassium Dippel had previously used, in purifying an oil obtained b distillation of dried blood. Instead of an improved crimso obtained a bluish mixture. He studied this phenomenon a and found that by calcining potash with dried blood product with water he obtained a lye which would give a to solutions of iron salts. This lye was called "blood lye."

He developed a successful process for making this n process was operated and kept a secret for about tw Woodward, an Englishman, published it. In Germany t known as Berlin blue, in England as Prussian blue, an purer quality was called Paris blue.

In 1752 Macquer found that by boiling Berlin blue w was a neutralization of the potash and iron hydroxide

new salt he at first called "phlogisticated alkali" and later named "blood lye salt." Today this is known as the "yellow prussiate of potash" or potassium ferrocyanide.

In 1782 Scheele produced hydrocyanic acid from Berlin blue and also from "blood lye salt." He described it in the language of the day as being composed of "volatile alkali," "aerial acid," and "phlogiston." Bergman thought the color was due to this acid and called it "blue acid."

In 1814 Gay-Lussac and Porret determined the composition of the ferrocyanides; the next year Gay-Lussac established the composition of the cyanides and Gmelin in 1822 that of the ferricyanides. Later Liebig cleared up the reactions relating to these, and Gentele and others developed the technical methods for the economic production of these various blue pigments in use today. The subsequent story of carbon and nitrogen is largely outside the field of paint but is closely related to Berlin Blue, and is dependent upon the knowledge of its constitution.

It is the story of a vast extension of organic syntheses, of the purification of illuminating gas, of the economic extraction of gold, and of the stability of nations, and last but not least the recovery of nitrogen from the air and its conversion into high explosives for use in national defense as well as in mining and road-building and the production of fertilizers to enrich our farms.

The Elements

Gold, silver, mercury, copper, tin, aluminum, zinc, lead, and carbon are the elementary pigments in common use today.

Gold, silver, copper, tin, aluminum, and some alloys are rolled and hammered until they are converted into brilliant flakes or fine powders which may be mixed with varnishes or lacquers ("bronzing liquids") and applied with a brush. These are known as "liquid gold," "liquid silver," bronze paints, etc.

Sometimes these metallic powders are blown or dusted onto varnished or lacquered surfaces while still "tacky," and are caught and held fast, thus producing a very brilliant coating.

Finely powdered zinc and powered lead are used for protective rather than decorative effect. Copper and mercury owing to their toxic properties enter into compositions used on ships' hulls to retard fouling by marine growths.

The element carbon is used quite extensively as a pigment. Graphite, a natural form of carbon, is found in many parts of the world. The crystalline varieties are less desirable as pigments than the amorphous. Some of the amorphous varieties ranging in carbon content from 95% to even less than 50% make excellent pigments. Artificial graphite made by heating anthracite coal in an electric furnace is equally good.

Lampblack, made from the smoke arising from inco
of oils, tars, pitches, etc., and gas black, a soot prod
gas by impinging a flame on a chilled surface, are impor
is estimated that in the year 1925, 140,000,000,000 cu
gas were burned in producing 177,417,378 pounds of ca
The larger part of this pigment is used in coloring ru
compounds although very large quantities are used in
inks.

Charcoal made from bone and consisting mainly of
and carbonate and carrying about 12% of carbon is
while charcoal made from wood although carrying
is less desirable.

The Sulfide Pigments

The sulfides of arsenic, antimony, cadmium, mercur
been used as pigments in paint. The sulfide of anti
vermilion is now used but little in paints, although it sti
use in rubber compounds.

Realgar and orpiment, the red and yellow sulfides
quently used in ancient times, find very little use in pai

Mercury sulfide, the natural cinnabar, long ago ce
mercial pigment but the artificial product known a
vermilion or Chinese vermilion is still used, althoug
than formerly.

Cadmium sulfide may be had in beautiful yellow
but is expensive and is not extensively used.

Zinc sulfide is a pigment of great opacity and in
barium sulfate or blanc fixe in the pigment known as
extensively used, especially in flat wall paints for i
In these paints it has recently very largely displaced w
oxide of zinc.

This pigment first made in France by De Douhet ab
developed in England as Orr's white or Charlton whi
twenty years has been improved still further, both in
United States, so that today it is a very important
this pigment is made as follows:

The mineral "barite" "barytes," "heavy spar," or "t
of barium sulfate ($BaSO_4$) ocurring in many lands, is crus
and mixed with pulverized coal. The mixture is he
revolving furnace, in the presence of a reducing atmosph

The resulting product is leached with water giving a s
be considered as being substantially barium sulfide,
pulverized coal, carbon, has burned at the expense of

$BaSO_4$ leaving BaS and forming carbon monoxide and carbon dioxide. A solution of zinc sulfate is prepared by one of several methods. It may be prepared directly from the zinc ore, zinc sulfide ("Sphalerite," "black jack," "blende") by a roasting process in which oxygen from the air combines with the ZnS forming $ZnSO_4$, or a solution may be prepared by treating metallic zinc with dilute sulfuric acid according to the reaction: $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$, or a solution may be made by treating zinc oxide with dilute sulfuric acid according to the reaction: $ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$. However, after the solution of zinc sulfate is prepared it is necessary to carefully remove all of those impurities which cause discoloration of the final product.

The barium sulfide and zinc sulfate solutions are next intimately mixed in a precipitation tub provided with facilities for stirring and heating.

The interesting reaction by which there is almost complete change from soluble to insoluble forms now takes place according to the equation:

$$\underset{\text{Soluble}}{BaS} + \underset{\text{Soluble}}{ZnSO_4} \longrightarrow \underset{\text{Insoluble}}{BaSO_4} + \underset{\text{Insoluble}}{ZnS}$$

This is one of the few technical operations in this industry in which the reacting chemicals are completely recovered in the product sought.

This precipitated pigment is now separated from the water, "mother liquor," by one of the modern methods of filtration, in some form of a filter press.

The press cake is dried and calcined in some form of a muffle furnace from which the oxygen of the air is excluded as much as is practicable. The process of calcining shrinks the pigment, increases its opacity and improves its stability. The calcined product is dropped from the muffle into water, best without coming into contact with air.

The wet pigment is finely ground in a buhrstone or ball mill or otherwise, and the creamy effluent flows to large washing and settling tanks. After being washed it is filter pressed, dried in drying chambers, and the dried product is milled, air floated, and packed in bags. All of this is not so simple as it sounds.

Great care must be exercised at every step. The chemicals must be carefully purified, contact with iron, copper and some other metals must be avoided, temperatures must be carefully regulated. There are unavoidable losses at every step, although as stated before the reaction is well-nigh perfect.

Notwithstanding the fact that all this care must be exercised and considerable capital invested in plant this wonderful and beautifully white pigment is the least expensive of all the opaque white pigments known, and today, in this era of high prices, it is quoted at less than six cents per pound. For use in interior painting it is almost indispensable but

conservative painters hesitate to recommend its gene
teriors.

The Oxides

Antimony pentoxide Sb_2O_5, under the name of "Tim
used to a limited extent. This is an attractive white pigme
is too costly to seriously compete with the other white p
general use.

Arsenic trioxide, white arsenic, As_2O_3, on account of its
is frequently used along with mercury and copper compoun
paints. White arsenic has no other value as a pigment.

The fouling of ship bottoms by marine, vegetable, and
is a very serious matter. In warm waters especially the
rapid unless a good antifouling paint is used. A ship, whos
encrusted with barnacles and seaweed, is slow and unma
quent docking and scraping of hulls is expensive but mus
unless a paint, which will retard or prevent fouling, is used.

Titanium dioxide or titanium white has been known f
century, yet it is only within very recent years that it has
mon use as a pigment. Titanium was first discovered
black sands of Cornwall by Gregor, an English clergyman.
the mineral in which it was found, menachite, and the elen
In 1795 Klaproth found titanium in the mineral rutile, a
the mythical giants. Later it was found that the elemen
Gregor was the same as that later discovered by Klaprot
titanium was retained.

Titanium occurs widely distributed in nature as rutil
ilmenite, $FeO.TiO_2$, or titanate of iron.

After many years of experimenting, commercial proc
developed for the production of pure titanium compounds f
ores of titanium. Norwegian and American chemists
leaders in this work.

"Titanox 25%," the best known of the titanium white pi
posed of about 25% titanium dioxide and 75% barium s
fixe. One process for preparing this pigment is somewhat
for lithopone.

Barium sulfide and titanium sulfate are allowed to react a
product is subjected to a process of calcination. This prod
white pigment of great opacity. This pigment is non-poiso
discolored by hydrogen sulfide.

Zinc oxide, zinc white, is a dazzling white pigment and a
member of the group of opaque white pigments. From 178
attempts had been made in France and England to bring it

in paint. Finally, Le Clair had good success in using it on public buildings, factories were established for its production, the price became cheaper, and its use became popular.

There are two manufacturing processes. In the French process metallic zinc is melted, in a suitable furnace, heated to boiling, and the vapors burn to zinc oxide. The white smoke travels through flues and cooling pipe lines to bags in a bag house. The white pigment collects in the bags while the hot gases pass through. The pigment particles are exceedingly fine, having been formed as a white smoke, and when pure metallic zinc is used the pigment is very nearly chemically pure zinc oxide.

In the American or Wetherill process the crushed and roasted (if a sulfide) ore is mixed with anthracite coal and charged onto a bed of burning coal in a suitable furnace. As the ore becomes heated the crude zinc oxide is reduced to metallic zinc, which vaporizes, and the zinc vapors burn in the heated zone above the charge. The zinc oxide smoke, and the products of combustion from the burning coal, travel together through flues and pipes to the bag house, as in the French process. This product contains slight impurities not present in French process product but is entirely satisfactory for most purposes.

Zinc-Lead White Pigments

Ore deposits of very intimately mixed sulfides of lead and zinc ore are found in various parts of the world. Before methods of selective flotation were developed some of these ores were of little use owing to the impossibility of economically separating the lead from the zinc. It was found that these mixed ores, after being carefully roasted, could be treated by a modified Wetherill process and a most excellent pigment could be obtained. These pigments vary in relative proportions of zinc oxide and basic lead sulfate according to the composition of the ore used.

A very useful and popular combination is one in which about two-thirds is zinc oxide and one-third lead sulfate. These zinc-lead pigments are rarely as white as zinc oxide but are excellent pigments possessing good opacity and some of the best properties of zinc oxide and white lead combined.

Oxides of Lead

Yellow oxide of lead (litharge, lead monoxide, PbO) is not suitable for use as a single pigment. It is lacking in good color and opacity and moreover reacts readily with linseed oil, and a paste or liquid paint made from it rapidly solidifies.

Some pigments retard the drying of linseed oil and to overcome this disadvantage litharge is sometimes added in small quantities thus producing paint which will dry satisfactorily. Litharge also is used in the preparation of varnishes, paste and liquid driers, boiled oil, etc. Red lead, usually

represented as Pb_3O_4, is used for the same purposes addition is used quite extensively as a pigment in pr structural steel.

Strictly speaking, commercial red lead is never Pb_3 mixture of Pb_3O_4 and PbO. A red lead containing m with linseed oil very much as litharge does, while a red free from litharge reacts very little with linseed oil. the only form of red lead which approached the comp made by very careful calcination of white lead and thi is known as orange mineral.

Litharge and ordinary red lead are made directly which is melted and is kept exposed to heated air while condition. Paints made from linseed oil and the best mineral will remain in workable condition in air-tight months while paints made from ordinary red lead will soli

Refinements in the process for making red lead hav a product almost equal to orange mineral in respect to linseed oil.

There are two oxides of copper which are used in a bottom paints. The black oxide, CuO, and the red oxi are toxic to marine vegetable and animal growths, especia

Oxide of mercury, HgO, made by a fire process is re a wet process it is yellow. Both of these varieties find paint on account of their toxic properties.

Iron oxides and hydroxides are found widely scatte along with carbon were the first pigments used by man.

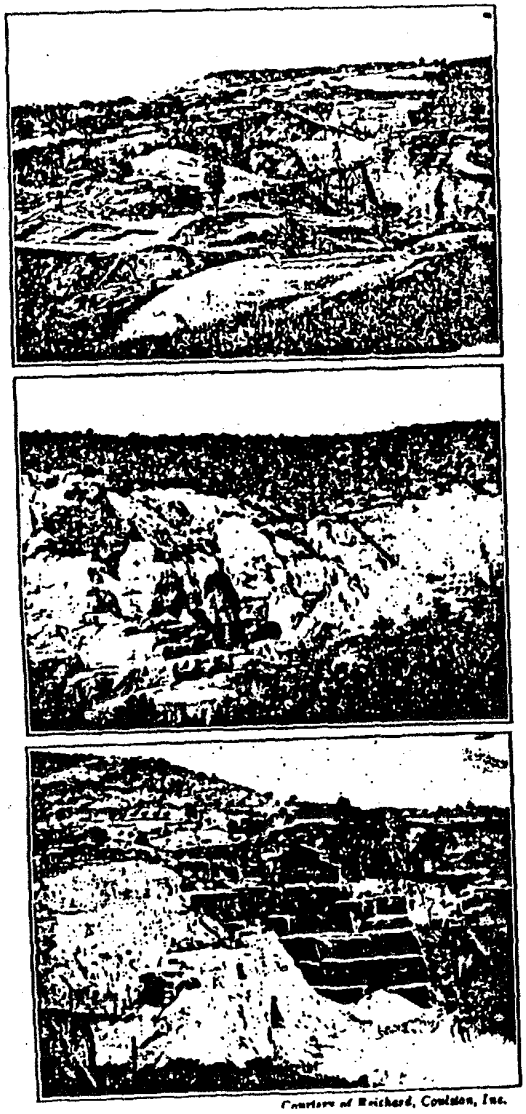
In the Isle of Cyprus, whence come some of our siennas, are still to be seen the workings which suppli Greeks, and Romans thousands of years ago.

The accompanying illustrations tell the story of ge and, with minor exceptions, the conditions of mining t much as they were four thousand years or more ago.

Yellow ochre of good quality may be obtained fro but the deposits are usually small and scattered. In there are enormous deposits of excellent quality. The tained both from open pits and subterranean workings. in edge roll mills, water-floated to separate it from ac and then settled in settling basins. The sediment is drie in the open air and sunshine or on shelves in drying houses

Ochres and siennas are very closely related and in their iron hydroxides to which their color is due. Raw um iron hydroxides associated with oxides and hydroxides of

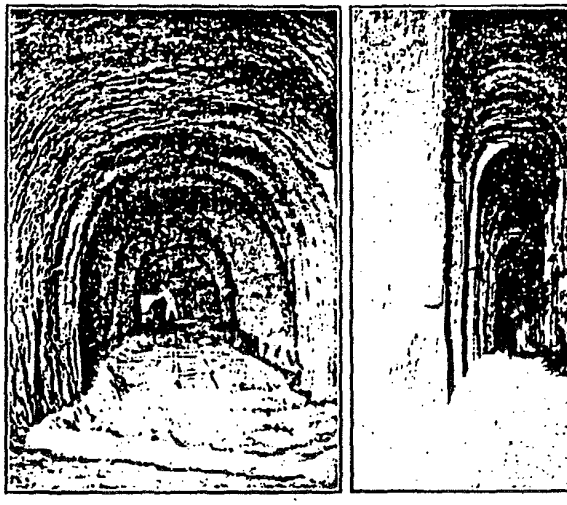
Yellow ochres and siennas become bright red when cal



Courtesy of Reichard, Coulston, Inc.

change to dark brown. By calcination the hydroxides chan
with the splitting off of water.

Ochres, siennas, and umbers have no definite chemical
Every kind of colored clay has been called an ochre and the ir
and oxide content may vary from a very few per cent to nea
dred per cent as in the hematites, which have sometimes been
A good quality of commercial French yellow ochre contains
lent of about 19% sesquioxide of iron, a raw Italian sienn

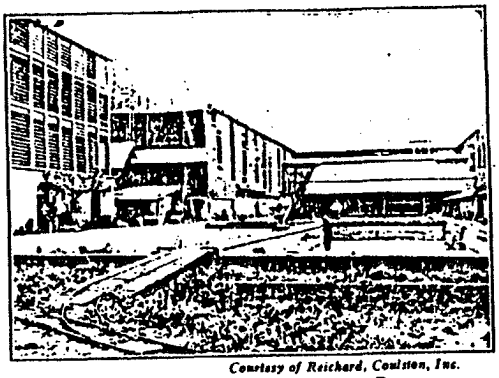


GALLERIES IN OCHRE DIGGINGS

70%, and an umber above 40%. The percentage is som
in the calcined products.

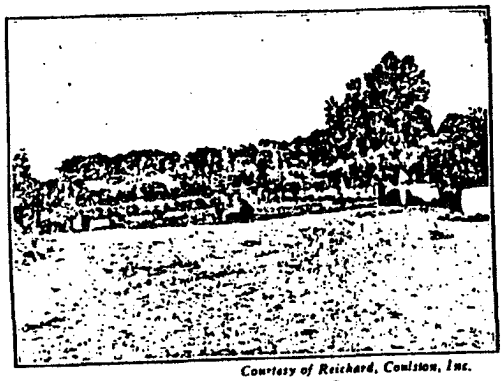
The mineral hematite, anhydrous sesquioxide of iron, Fe_2O_3, color from bright red to nearly black is always red when finel Persian Red and Indian Red are excellent hematite pigmen taining about 95% of Fe_2O_3.

Natural carbonate of iron, siderite, $FeCO_3$, or spathic iron hydrated sesquioxides (hydroxides of iron, such as the limo iron ores, are of especial interest to the paint industry, since b these minerals yield sesquioxide of iron pigments of various h milling properties).



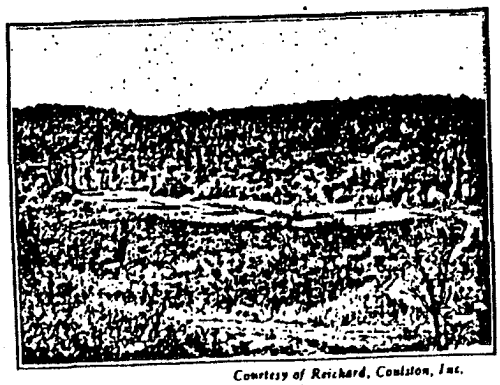
Courtesy of Reichard, Coulston, Inc.

OCHRE DRYING SHEDS AND WASHING PONDS



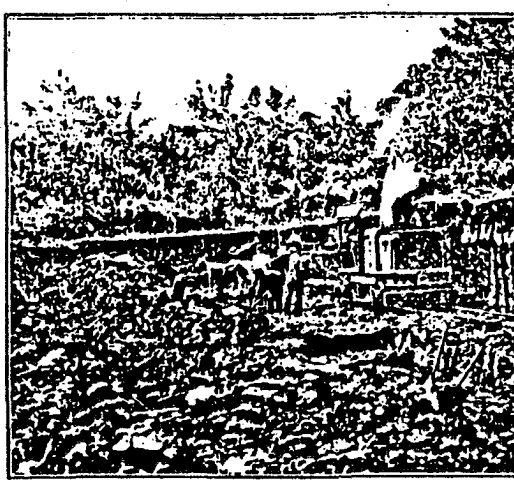
Courtesy of Reichard, Coulston, Inc.

A FRENCH OCHRE DRYING GROUND



Courtesy of Reichard, Coulston, Inc.

The accompanying illustration is of a bog iron ore dep
Ontario, owned and operated by the Canada Paint C
in its crude state is contaminated with peaty matter a
use in paint. However, when calcined, "burned" in a
simple construction in which the flame and heated ai
to shelf over the mineral, a most excellent pigment is ob
range of hues is obtained by varying the temperature
cination. This type of pigment cannot be surpassed in re
and working properties and the only limitation on its



Courtesy of the Can

BOG IRON ORE, RED MILL, ONTARIO, CANADA

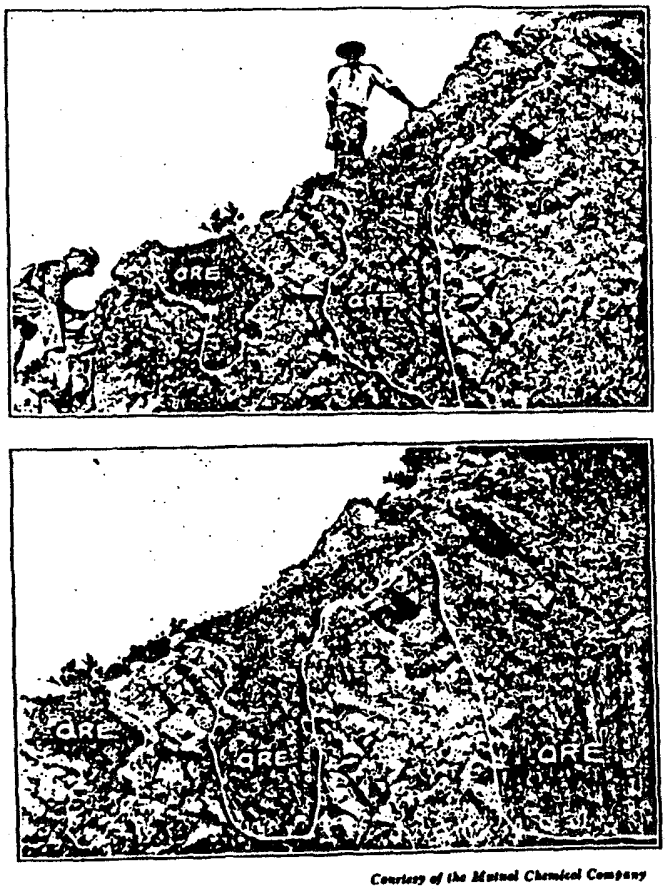
A somewhat brighter red and considerably more expens
iron pigment is made by calcination of green vitriol, ferr

The mineral magnetite, Fe_3O_4, black oxide of iron, is
pigment on account of the difficulty in grinding it sufficie

A black oxide of iron pigment Fe_3O_4, made from the r
heating in a furnace in the presence of reducing gases, ha
paint.

Chromite, or chrome iron ore, $FeCr_2O_4$, is found in ma
only a few deposits can be profitably worked at the pr
supply comes principally from Rhodesia, New Caledonia, I
Cuba.

To obtain the chromium pigments the chrome iron
finely pulverized and intimately mixed with quicklime



Courtesy of the Mutual Chemical Company

CHROME ORE DEPOSITS IN NEW CALEDONIA
Views of Side Vein on 1 and 2 Levels, Fantoche Mine. Note Altitude of Ore.

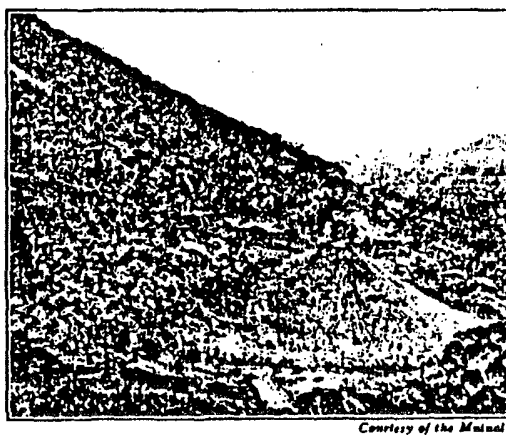
bonate and roasted in a reverberatory furnace. The roasted product is leached with water, the chromium passing into solution as sodium chromate. From this sodium chromate many chrome pigments are made.

There are two well-known oxides of chromium. Chromium sesquioxide, Cr_2O_3, is a dull green substance which is easily converted into a fine powder making an excellent pigment. This is a true chrome green which is ab-

solutely fast to light, but owing to its high cost and lack of
but little in paint. The chrome green of commerce is a n
yellow and Prussian blue, possessing great beauty an
alas, not the permanency of chromium sesquioxide.

The other oxide of chromium, CrO_3, chromium trioxide,
of chromic acid is not used as such in paint but enters int
of the chrome yellows, oranges, scarlets, and greens.

Chrome yellow or chromate of lead is a beautiful and
pigment. The normal chromate of lead, $PbCrO_4$, is
yellow." The basic chromate of lead, $PbO.PbCrO_4$, is



Courtesy of the Mutual

CHROME MINE IN NEW CALEDONIA

or "American vermilion." Products intermediate in
"chrome oranges," the more basic the pigment the deepe
and vice versa. Chrome yellows, lighter in tone than "
"light," "double light," etc., are usually prepared by co-p
the chromate of lead varying amounts of sulfate of lead.

The green pigment which is used to the largest extent is
This is a mixture of chrome yellow and Prussian blue
practice to prepare chrome yellow in one tank and Pr
adjacent one.

At the proper time the two are run together into a lar
below, thus producing a very intimate green mixture.
filter-pressed, dried and pulverized, and marketed as c.
Greens of weaker tinting strength are made by adding

clay, silica, or other translucent white pigments to the C.P. green in the tank before filtration or the press cakes of C.P. green may be mixed with these translucent pigments in edge roll mills or otherwise.

By varying the proportions of chrome yellow and Prussian blue many beautiful tones of green are obtained.

The chromates of strontium, barium, and zinc are used as pigments to a limited extent.

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E. C. HOLTON, THE SHERWIN-WILLIAMS COMPANY, CLE

White lead or basic carbonate white lead is the one ou white pigment of the centuries. Known to the ancient G it has come down through the ages and is today certainl and most popular opaque white pigment.

Volumes have been written on this pigment and it will c here that in spite of the facts that it is rather poisonc legislated out of use in some countries, that it is darkened that it lacks the dazzling whiteness of zinc oxide and li opacity is less than that of titanium pigments; neverth of its general usability and the uniformly good results ol under normal conditions, it still enters largely into the c best white paints and light tints used for outside paint

This white lead, which is generally represented as appr position of $Pb(OH)_2 \cdot (PbCO_3)_2$ is often called Dutch Lead years the industry throve in Holland and pigment made took their name. In France, Germany, England, an and quicker processes have been developed and the pro various names. Many of these are fully equal to the thing but whiteness in which they often are superior.

In addition to the basic carbonate there is another wl lead which has been extensively used as a pigment. Th of lead or basic sulfate white lead or sublimed white lea is made by a fire process in which lead sulfide ore, galena and vaporized in a suitable furnace and the lead sulf through a cooling system of pipes to the collecting chambe excellent pigment and is not to be confused with a lead su a by-product in wet processes. Since galena frequently sphalerite the sublimed lead usually consists of basic su five per cent or more of zinc oxide. Thus it happens th white fume pigments we have zinc oxide free from lead, ing small quantities of lead, zinc oxide—lead sulfate pi from 50–50 composition to 75–25; sublimed lead or bas carrying 10% or more of zinc oxide or lesser amounts ev traces.

There are two blue pigments which are used very e These are Prussian blue and ultramarine. As already made the first Prussian blue but his blue was not so pure as the blues of today. Prussian blue is essentially fe yet it contains closely associated with it small quantities potassium, or ammonium compounds. The usual met

it is to add a solution of sodium or potassium ferrocyanide to a solution of ferrous sulfate. There is formed a nearly white precipitate of ferrous ferrocyanide, which when exposed to air or oxidizing chemicals, rapidly becomes blue.

Blues vary in color tone, and intensity according to the nature of the oxidant used and the method of procedure. This is an art in itself which would require a volume to describe but it can be stated in general that air oxidation is not satisfactory and that careful washing is essential. A somewhat similar blue may be made by reacting on a ferrous salt with a ferricyanide. This is sometimes called Turnbull's blue.

Both ferric ferrocyanide and ferrous ferricyanide are frequently if not always present in Prussian blue. For more than two hundred years this beautiful and intense blue has been preëminent. In mixture with chrome yellow it forms our most important green pigment, chrome green.

In the early part of the last century chemists succeeded in developing processes for the manufacture of the beautiful pigment ultramarine, the equivalent of the very expensive lapis lazuli, which it has displaced. Here again was illustrated the keen scientific and commercial rivalry between two great nations. The prize offered by the French Societe d' Encouragement was given to Guimet of France although many believed it rightfully belonged to Gmelin of Germany. This blue is not injured by alkali but is quickly destroyed by acids whereas Prussian blue is destroyed by alkali and is rather resistant to acids.

Translucents

Non-opaque white pigments or translucents are those colorless pigments whose indices of refraction are so close to that of the paint vehicles that when made into paint they offer but little obstruction to the passage of the visible light rays.

Among the silicates those in common use are silica (SiO_2), clay, hydrated aluminum silicate, asbestine (essentially a magnesium silicate), and other white silicates of the amphibole, serpentine, and talc groups.

Of the carbonates, calcium carbonate is the most extensively used. Whiting is usually made from chalk by wet grinding in edge roll mills and water floating to separate it from the accompanying siliceous particles. Ground limestone is usually made by dry grinding in impact mills and is air floated. Barium carbonate is used to a very limited extent. This is usually prepared by chemical precipitation from barium sulfide solution. Magnesium carbonate also has a limited use. This also is usually obtained by chemical precipitation.

In the sulfate group barium sulfate is most extensively used. The mineral barite is crushed, then finely ground and air floated. Sometimes it is necessary to remove traces of iron oxide with which the mineral is stained.

These are removed by treatment with sulfuric or hy
subsequent careful washing with water. The pigment
Blanc fixe, a chemically precipitated barium sulfate is us
in paint mixtures, but as a component of composite pig
pone, titanox, and various lake pigments it is usec
Hydrated calcium sulfate, gypsum ($CaSO_4 \cdot 2H_2O$) is u
less than formerly.

These non-opaque or translucent white pigments,
priced than white lead, have sometimes been regarded a
worthless adulterants because when used with white
creased the weight and bulk of the paint and decreas
so far as white paint alone was concerned, and duri
oxide of zinc and white lead were the only opaque wh
there was some justification for this opinion. With c
always been a different matter.

Very few of the beautiful lake pigments could be m
of one or more of these translucent pigments and ev
made some of them would be too expensive to use.
chrome yellow, chrome green, Prussian blue, etc., are
and their use would be greatly curtailed if it were not
pigments, which have nearly all the desirable pigme
opacity and color. Fortunately, these translucent p
less expensive than the brightest and gayest colors. N
translucency they may be mixed with these colors wit
brilliancy and without changing their tones and this
plished with opaque white pigments. Much of the
today is due to the use of the translucent pigments.

Natural Organic Colors

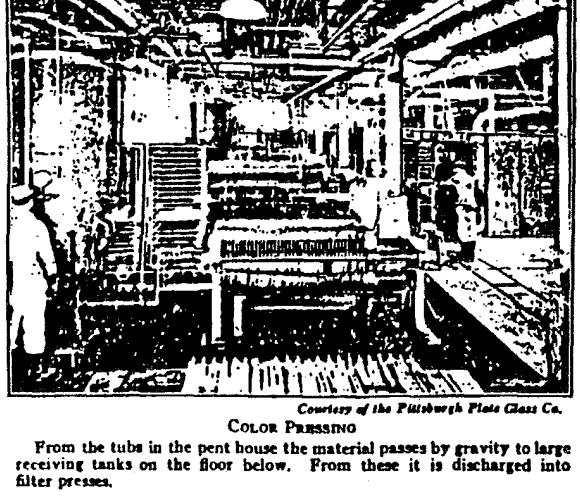
Until recently various natural organic coloring matte
ally used, although in small quantities. Of these the b
and carmine and Indian yellow. Many natural dyes
wood, bark, roots, and berries have been used in ma

The general procedure was to extract the dyestuff
which it occurred. To the water solution of this dy
alum was added and then a solution of alkali or alkali
usual result was that a considerable part of the color
of it, was precipitated along with the aluminum hydr
or in some cases chemical combination. Many reci
for the use of various metallic salts, and other chemicals
results. These products were called lakes. For use
customary to have whiting, silica, barytes, or other
pigment present in the precipitating mixture. In thi

Courtesy of the Pittsburgh Plate Glass Co.

COLOR "STRIKING"

Each set of precipitating tubs has a corresponding tub in the pent house.



Courtesy of the Pittsburgh Plate Glass Co.

COLOR PRESSING

From the tubs in the pent house the material passes by gravity to large receiving tanks on the floor below. From these it is discharged into filter presses.

precipitated on, and in drying became firmly attached substratum. The best-known lakes were made from ma Brazil woods, and Persian berries.

The natural organic colors and dyestuffs have now beer superseded by the synthetic colors.

Synthetic Colors

With the discovery of mauve by Perkin, and the subs velopment of the synthetic dyestuff industry, it was to l attempts would be made to utilize these new dyes in the A satisfactory pigment must be insoluble in water and in t used. Many of the new dyes are soluble in water, othe alcohol, or oil, or other paint vehicles. Some of these d their respective solvents, have found use as stains but o are reasonably fast to light can be recommended. If the as pigments they must first be made insoluble.

We have already seen that lake pigments made from co Brazil wood, Persian berries, etc., have long been used in th With the experience already acquired and with the bett the constitution of the new dyes it became possible for t to work more intelligently. The first basic dyes of the tr group were usually fixed by tannic acid, picric acid, arsen more recently by tungstic acid, etc. Dyes of the eosin gr precipitated as insoluble lead lakes. Dyes in which there sulfonic groups are usually precipitated as barium and calci in which there are hydroxyl groups are usually converted and chromium lakes. It frequently happens that a dye ha ings in its molecule and each of these is taken care of by it tant. Usually these dyes have commanded a high price of their intense coloring power it has been possible to m lake pigments by precipitating a small quantity of dye on pigments.

Of the non-opaque pigments china clay, barytes, blanc singly or in mixtures, are most extensively used. Som are precipitated directly on the opaque pigments but mor above-described lakes are used in mixture with the opa

One class of dyestuffs which has assumed great importa industry is that of the azo pigments made by coupling *be* the diazonium compounds of *para*-nitroaniline; *meta*-ni and similar compounds. The former, *para*-nitraniline re helio fast red or toluidine toner, are the reds so commor cultural implements, vehicles, toys, etc.

The synthesis proceeds as follows:

BY-PRODUCTS FROM THE COKE AND ILLUMINATING GAS INDUSTRIES

Toluol	*Naphthalene*
Treatment with mixed nitric and sulfuric acid	Treatment with sulfuric acid
↓	↓
para-Nitrotoluol	Naphthalenesulfonic acid
Treatment with iron filings and hydrochloric acid	Neutralization with sodium chloride
↓	↓
para-Toluidine	Sodium Naphthalenesulfonate
Treatment with acetic acid	Fusion with caustic soda
↓	↓
Aceto-*para*-Toluide	Sodium *beta*-Naphtholate, crude
Treatment with mixed nitric and sulfuric acid	Treatment with dilute acids
↓	↓
meta-Nitro-aceto-*para*-Toluide	*beta*-Naphthol, crude
Treatment with caustic soda	Distill
↓	↓
meta-Nitro-*para*-Toluidine	*beta*-Naphthol, pure
Treatment with sodium nitrite and hydrochloric acid	Dissolve in water with caustic soda
↓	↓
Diazonium compd. of *meta*-Nitro-*para*-Toluidine	Sodium *beta*-Naphtholate

↘ ↙

Mix

and coupling takes place

↓

meta-Nitro-*para*-Toluene-azo-*beta*-Naphthol

or

Helio Fast Red; Toluidine Toner; etc.

This is a beautiful scarlet pigment, practically insoluble in water and but slightly soluble in ordinary oil and varnish paints, and reasonably fast to light. It may be used by itself or in mixture with many other pigments.

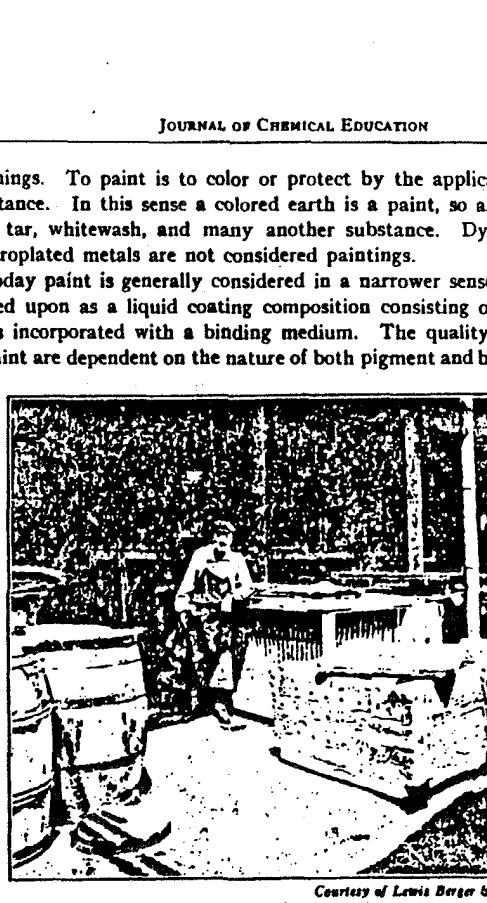
The eosines and xylidine scarlets were used quite extensively some years ago but are now almost entirely superseded by the two reds just mentioned. From the synthetic alizarines, which have superseded the natural madder, lakes of very great light fastness are made and used to a considerable extent. The use of synthetic indigos, the indanthrenes, and the very fast vat colors is slowly increasing.

What Constitutes a Paint or Varnish?

In its broadest sense a paint has been considered as a coloring or protective substance which may be easily and quickly applied to the surfaces

of things. To paint is to color or protect by the applic substance. In this sense a colored earth is a paint, so a coal tar, whitewash, and many another substance. Dy electroplated metals are not considered paintings.

Today paint is generally considered in a narrower sens looked upon as a liquid coating composition consisting o ticles incorporated with a binding medium. The quality of paint are dependent on the nature of both pigment and b



Courtesy of Lewis Berger &

OLD-STYLE FILTERING BOX

A section of the dry color department of Lewis Berger & S London (England) in 1900. This plant has a business histo two centuries and the color maker shown had been in its emp years at the time the picture was taken. In the foreground is old type of filter press. The wet color is wrapped in linen cl into the square box, and pressure is applied by placing squar on top; the escaping water passes through the apertures arou

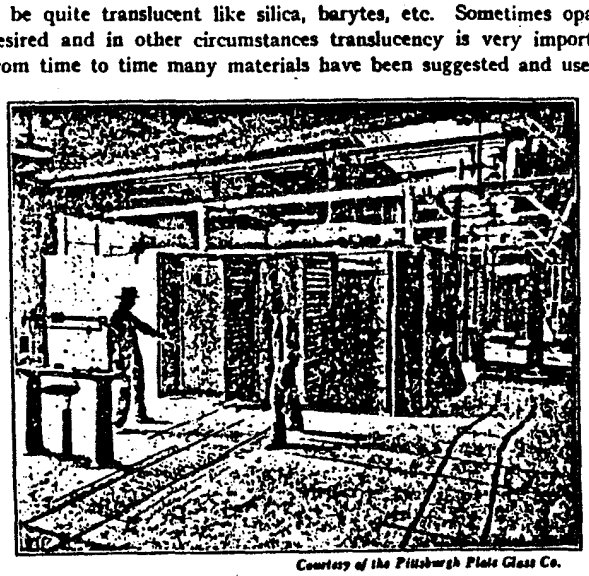
When the binding medium is a liquid the liquid portion usually referred to as the vehicle and the solid portion is ment.

Pigments may consist of finely divided metals such as gold etc., or various mineral substances found in nature such as cinnabar, lapis lazuli, barytes, silica, etc., or chemically pr substances such as white lead, chrome yellow, zinc white o made from natural organic coloring matters such as madde

or from synthetic coloring matters such as the eosines, the azo pigment colors, the indanthrenes, the alizarines, etc.

The pigment particles usually possess distinctive and desired color such as carbon, black; vermilion, red; ultramarine, blue, etc. If colorless or white, such as zinc oxide or white lead, they have great opacity or they may be quite translucent like silica, barytes, etc. Sometimes opacity is desired and in other circumstances translucency is very important.

From time to time many materials have been suggested and used as



Courtesy of the Pittsburgh Plate Glass Co.

COLOR-DRYING

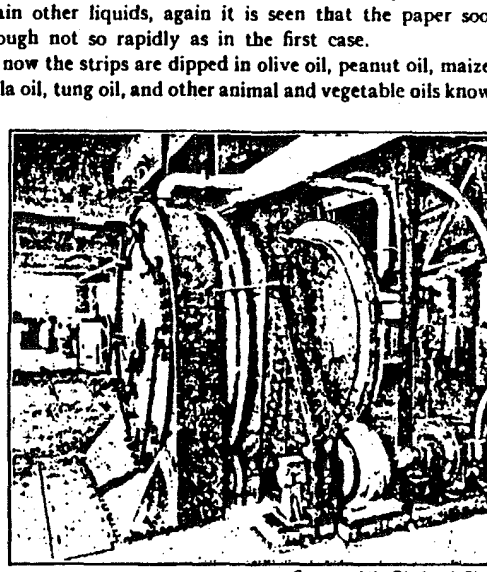
The material removed from the filter presses is placed on trays on racks and taken to the driers. After drying, each rack is passed over a floor scale to weigh the contents.

binding materials for pigments to be used in painting. Formerly waxes were quite generally used. Pigments were mixed with melted waxes and the paint was applied in a melted condition. Vehicles have been made from egg yolk emulsion; white of egg in solution in water; solution of gelatin; water glass solution; water solution of gum, glue, honey, starch, etc., lime water; solutions of resins and waxes in volatile solvents; solutions of resins and drying oils in volatile solvents; drying oils; solutions of cellulose compounds in volatile solvents, etc.

To understand paint, varnish, lacquers, etc., it is necessary to understand what drying is. If strips of paper are moistened by dipping them in different liquids and if they are then hung in the air to dry certain differences may be observed. Papers dipped into ether, alcohol, chloroform,

gasoline, benzine, benzol, ethyl acetate, etc., when exp
rapidly become dry and, except for traces of odor in some ca
be no certainty as to which strip had been moistened by a
If paper is moistened with water, kerosene oil, pine oil, an
certain other liquids, again it is seen that the paper soo
although not so rapidly as in the first case.

If now the strips are dipped in olive oil, peanut oil, maize
perilla oil, tung oil, and other animal and vegetable oils know



Courtesy of the Pittsburgh Pla

COLOR DRY BLENDING

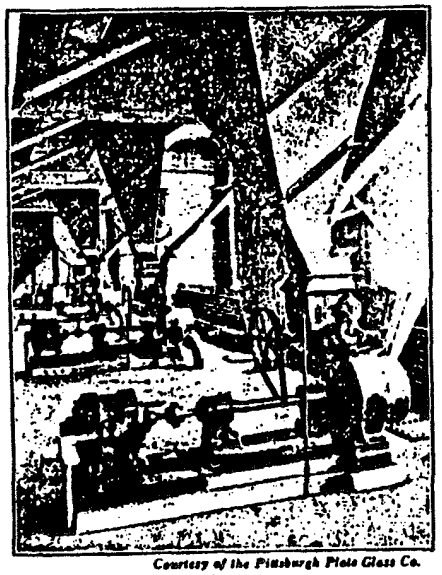
**With this apparatus, which holds two to four tons, conte
several different batches are mixed together, resulting in a de
formity heretofore unobtainable.**

great differences are seen. These oils do not disappear.
the paper continues to be oily for a considerable time.
or so the tung oil changes its appearance, becomes less o
crinkly surface, and becomes solid or dry. It has disap
the sense that it has changed from the liquid to the soli
two or more days the perilla and linseed oil act in a somewh
although they do not develop so crinkly a surface, and f
solid or "dry." The maize, olive, and peanut oils do not
a few days. They thicken somewhat, the maize oil sho
toward drying while the olive and peanut oils remain oi

In the paint, varnish, and lacquer industries those liquic
like water, alcohol, spirits of turpentine, etc., by disappe

air as vapors are called volatile solvents. Those animal and vegetable oils which do not disappear as vapors but become "dry" by solidification are called drying oils. Those oils which remain oily or greasy indefinitely are called non-drying oils. Other oils which dry very slowly are called semi-drying oils.

In this country three vegetable drying oils are extensively used in paints and varnishes. These are linseed oil, China wood oil (tung oil), and perilla oil. Other vegetable oils such as castor oil, soja bean oil, poppy seed oil, and some others are used in much smaller quantities. This also holds for menhaden fish oil and other marine animal oils.



Courtesy of the Pittsburgh Plate Glass Co.

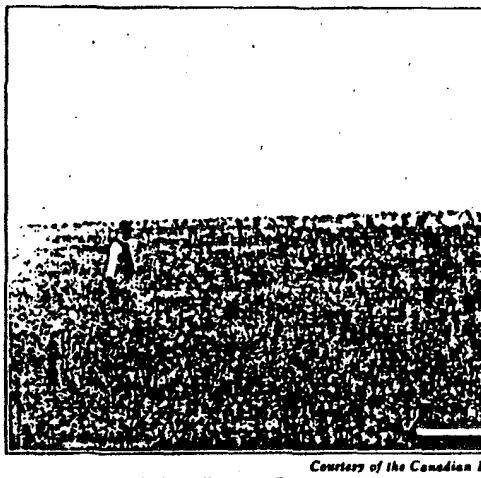
DRY GRINDING

The material passes from the blender to the hopper and then to the pulverizer.

The best known drying oil, the oil which has been used in painting to a greater extent than any other, is linseed oil, the oil of flax seed. Flax, the *linum usitatissimum* of the Romans, is extensively cultivated in many parts of the world. India, Russia, Argentine, the United States, and British North West are the principal producers. The seed is carefully cleaned and freed from foreign seeds, crushed, usually steamed, then subjected to great pressure in hydraulic presses. The expressed oil is carefully filtered and is ready for use as raw linseed oil. Raw linseed oil when exposed to the air in a thin film becomes solid or dries in about 72 hours.

This drying may be considerably hastened by the addition of substances known as driers. Compounds of lead, manganese, and cobalt are commonly used for this purpose. The most active driers are made by forming oil-soluble compounds of one or more of these metallic elements. These driers are usually made by heating the oxides of these elements with linseed oil and resins in a kettle. A concentrated drier made in this way although liquid when hot, solidifies on cooling, and is inconvenient to use;

therefore, it is customary to dilute this with spirits of tur troleum solvent and the resulting product is known as a common strength of liquid drier is one that will cause a to dry in 10 hours or less when 5 to 10% of liquid drier with it. Sometimes it is desirable to hasten the drying of out the use of volatile solvents and resins. To accompli oil may be heated ("boiled") with the drying compounds a small amount has dissolved in the oil. The oil thus pr



Courtesy of the Canadian

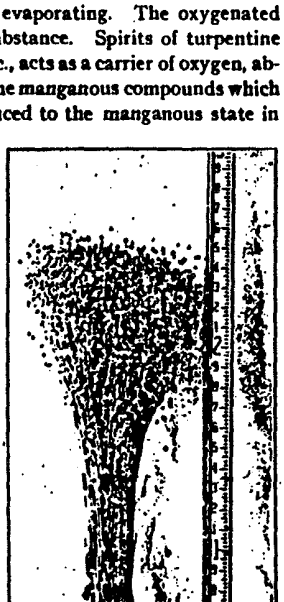
A FLAX FIELD IN SOUTHERN MANITOBA

"boiled oil" and should dry in about ten hours. This "b boiled with driers, is somewhat darker, a little heavier, limpid than raw oil.

When linseed oil is carefully heated in a kettle, without ually thickens, without discoloration, until quite viscous, heating may be continued until it is nearly solid, the pro in color until of an amber tone. These thickened oils a graphic varnishes and enter largely into lithographic inks varnish paints.

In the course of time it was discovered that the resinou the coniferae when boiled with water or treated with st volatile liquid which we now call spirits of turpentine. Th played a very important rôle. It is an excellent solvent fo and recent resinous exudations from trees. Freshly distille

pentine evaporates completely from a strip of paper, dipped in it and then exposed to the air, in about seven minutes. Exposed to the air in bulk, a portion absorbs oxygen, while the rest is evaporating. The oxygenated portion gradually changes to a resinous substance. Spirits of turpentine when mixed with linseed oil, liquid driers, etc., acts as a carrier of oxygen, absorbing it from the air and delivering it to the manganous compounds which become manganic. These in turn are reduced to the manganous state in the oxidation of the linseed oil. Thus in addition to being an excellent solvent spirits of turpentine is a useful catalytic agent in the paint and varnish industry.



Courtesy of the Canadian Pacific Ry.

A SHEAF OF FLAX

Fossil resins or those resins which have laid in the ground for long periods of time and have undergone a considerable change in their chemical composition usually are insoluble in linseed oil and spirits of turpentine either separately or in mixture. If these resins, however, are heated and partially decomposed, yielding water, terpenes, etc., amounting to twenty per cent or more of their original weight, the residual resin becomes soluble and is suitable for use in varnishes and lacquers.

A film produced by the drying of raw linseed oil is rather soft and possesses little luster. A film produced from oil to which liquid drier has been added is firmer and more lustrous. An oil boiled with driers also gives such a film.

Varnishes

For many purposes it is desirable to have a finish of even greater hardness and deeper luster. This is obtained by the use of varnish or rather oil-resin varnish which is a composition of a drying oil, a hard resin, and a volatile solvent. The best varnishes of recent years have been varnishes of this type in which linseed oil, or other drying oil, heated to approximately 600°F. is mixed with a fossil resin which has been melted at this or even higher temperatures and kept hot until it has changed to a condition in which it is soluble in linseed oil and spirits of turpentine mixtures. In this country when we use the single word varnish, this type of varnish is usually understood.

A long oil varnish is one of this type in which the amoun
nearly equals or exceeds the quantity of resins used and a sl
is the converse of this. Generally speaking, the long oil var
durable than the short oil varnishes while the latter have
than the former. There are many varieties of oil-resin v
ing in their properties according to variations in qualities
of oils and resins employed.

The pine forests of our southern states have supported
industry for many years. The gum turpentine, which f

Courtesy of the Turpentine Rosin Produc

TURPENTINE DIPPING

The gum or "dip" as it is called, flows over the face to the c
the cup is filled it is emptied or "dipped" into buckets, then i
(50 gallons each) and hauled to the still. The dip is a solution
acids in spirits of turpentine. The stilling vaporizes the spirits
behind the resin acids or "rosin."

incisions made in the bark of the trees, is collected and c
where the spirits of turpentine is driven over with steam,
collected, and the residue in the stills becomes the rosin o
trade. This rosin differs greatly from the hard fossil resin
nishes formerly made from it were unsatisfactory, since the
in hardness and durability. Fortunately processes have b
for the commercial production of very durable glycerol an
of rosin which when combined with China wood oil and linse
varnishes of the highest quality.

The fossil resins have come to us mainly as follows: amber from northern Europe, copals from East Africa and West Africa, the East Indies, southern Asia, New Zealand, and the Philippines. For the last forty years the most popular varnish resin has been the New Zealand kauri. With the gradual exhaustion of the known New Zealand deposits the use of copals from the Belgian Congo has greatly increased. The glycerol esters of rosin which are made from rosin and glycerine by a condensation and splitting off of water are entering into serious competition with the fossil resins.

The synthetic phenol-formaldehyde resins and other related compounds and the *para*-coumaron resins made from coal tar distillates are also beginning to displace the natural resins in varnishes.

In addition to this usual varnish of commerce, *i. e.*, the oil-resin varnish, there are other varnishes such as the natural varnishes consisting of the sap or juice of certain trees growing in Oriental countries. The lacquers of China, Japan, and India are of this class. There is also a class of varnishes known as spirit varnishes. These varnishes are ordinarily made by dissolving a resin or a mixture of resins in a volatile solvent such as spirits of turpentine, or benzol, or petroleum distillate, or alcohol, or ether, or ester, or ketone, or a mixture of two or more of these solvents. These are sometimes dissolved without heat, "cold cut," or the solvents may be added to the resins after simply melting them, or in the case of some fossil resins it becomes necessary to first fuse and partially decompose them until they become changed into soluble resins. Shellac mastic, dammar, sandarac, and spirit-soluble manila are the resins most frequently used in these spirit varnishes. Synthetic resins of the phenol-formaldehyde type are also being used in this way. Spirit varnishes containing little of the resin and much of the solvent have frequently been called lacquers.

Cellulose varnishes constitute another class which differs from the older type of spirit varnish in that instead of a resin a compound of cellulose is used. This class is subdivided into cellulose acetate varnishes and nitrocellulose varnishes, the latter being also known as pyroxylin varnish, zapon varnish, celluloid varnish, etc. These cellulose spirit varnishes have also been called lacquers. As already stated, lacquers heretofore usually have been considered as those varnishes which produce a very thin, hard, lustrous coating. The term "lacquer" is being used very generally today to include both quick drying varnishes and quick drying paints in which more or less low-viscosity nitrocellulose is used.

Although varnishes are usually classified as outlined, the dividing lines are not sharp. An oil resin varnish having very little oil and much resin may be considered as a spirit varnish to which a little oil has been added. In the same way cellulose spirit varnishes merge into resin spirit varnishes, in some there is more of the cellulose ester and less of the resin while in others the converse is true.

For many years spirits of turpentine was the one pre
and reducer for paints and varnishes. Solvents such a
zine, kerosine, etc., were prepared from petroleum by dist
zol, toluol, and other solvents were distilled from coal t
obtained from the illuminating gas industry but there
against the use of any of these. With the rapid growth of
paint industry in the United States it became evident th
pentine would soon be exhausted and distillers of petr
ceeded in supplying the industry with petroleum solvents
purposes satisfactorily displace spirits of turpentine.