The Materials of Paint Manufacture

An Address by

G. B. HECKEL

Before the Section of Physics and Chemistry at the Franklin Institute, Philadelphia

June, 1910

(Revised and Extended February, 1928)

Published by the
Educational Bureau, Paint Manufacturers' Association of the United States, and National Varnish Manufacturers' Association
Secretary's Office: 800 The Bourse, Philadelphia, Pa.

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"Prepared Paint is not only a product of Science and Civilization but is also a result of Progress and Evolution."

PREFACE

The address which constitutes the main text of this pamphlet was delivered before the Franklin Institute during the spring of 1910. The demand for copies quickly exhausted the supply of reprints from the "Journal of the Franklin Institute." It was then reprinted in its original form, illustrated by reprints of some of the more important lantern slides shown in connection with the address. (Over 100 of these were shown.)

The pamphlet has attained some popularity in the trade, but more especially with educators, who are seeking information on the subject in a convenient and presentable form.

This demand has again exhausted the supply of the second reprint and a new edition has become necessary. But in the fifteen years that have elapsed since the delivery of the original lecture, paint technology has advanced amazingly, and while the original statements may stand practically unchanged, they no longer adequately cover the subject. It has, therefore, seemed advisable to expand the text by including some additional matter as well as to make some slight revision of the original text.

The object of this publication is to remind paint manufacturers, paint salesmen, painters and paint dealers that the product in which they deal is an important one and that their calling is dignified, and to help educators in placing the essential facts of paint manufacture before their students in intelligible form.

Tennyson makes the hero of the poem

"Locksley Hall" designate himself—

> * * * the heir of all the ages, in the foremost files of time."

The man that deals with familiar and commonplace paint can justly regard himself as the legatee of science, industry, exploration and research dating from the days "when Adam delved and Eve span."

But, in a special sense, modern science has produced modern paint. The history of the materials used in producing it are veritable "Fairy Tales of Science." Consider, for instance, the venerable antiquity of white lead (Cerussa) and lamp black; the aboriginal associations of iron oxide and ochre; the century-old controversy over zinc oxide. Reflect upon the tragic romance of Madder and Indigo. Ponder over the marvels of the coal tar dyes.

The histories of the individual pigments are also full of romance: there is our familiar Prussian blue, for example, discovered through a blunder of the German color maker, Diesbach, who in making a Florentine lake accidentally used an alkali that had previously been used in clarifying ox-blood; there is ultramarine blue, the production of which was due to the hint obtained from the accidental blue noticed from time to time in soda furnaces; there is American process or direct zinc oxide, which resulted from long-continued and costly attempts to utilize Franklinite as an iron ore.

In the following paper, only the most salient points of interest are touched upon, but even

from this brief summary those who have never been struck by the fact, must realize that paint—the common paint which we buy in the stores and rub off on our clothes—

> Hath had in other worlds its setting
> And cometh from afar.

The Dakota farmer who paints his barn with it, paints with a product of the flax from his own fields; the Florida "cracker" who daubs his shack with red paint, brings back to the pine forest its own product; the western miner paints his lean-to with the product of the neighboring mine—there is scarcely any quarter of the globe to which some portion of the paint can or its contents does not "return home." All science has contributed to its production and each quarter of the globe has furnished some ingredient.

Consider also the utility of this can of "ready-to-use paint." Ingeniously devised and perfected machinery has ground and blended the materials; apparatus almost human in its uncanny ingenuity has made, sealed and labelled the can; the railway has brought it to the neighboring dealer's shelf; it is there, cheap, convenient, excellent, for instant use. Suppose that the chemist, the inventor, the machinist, the importer, the manufacturer had not done this preliminary work, where would be the paint and where the painter? To appreciate the situation we have only to read the notes left us by some of the great artists of the Renaissance, who made their own colors and vehicles and whose works, darkened, cracked and defaced, now hang as relics of past beauty in the galleries of Europe.

Paint is the cheapest and handiest convenience of modern times. It costs nothing because it saves more than it costs. It is the only means by which our investment in perishable structures can be conserved. It comes to us practically complete and it enables us to pass our lives in clean, sanitary, durable and beautiful surroundings.

The Materials of Paint Manufacture

By G. B. HECKEL

During recent years we have become somewhat familiar with the term "Scientifically Prepared Paint," and have heard or read some

Linseed Oil—Flax in Bloom

controversy over the propriety of the term. I hope to show before I finish that the term is justified and that prepared paint is not only a product of science and civilization, but that it is also a result of progress and evolution, as much as any other modern product.

An English writer has said of paint making that it was first an art, then a trick, but that now it has become a science. I have here a relic of the earliest known American Paint Makers—probably the same people who built the mysterious mounds of the Mississippi Valley. It is an axe or hatchet of hematite, and if properly crushed and ground would make a good grade of iron oxide pigment. It was found in a tunnel uncovered at Lesley, Missouri, by modern miners who are still taking oxide from the same vein. Iron oxide was one of the pigments known to the aboriginal. He reduced the native hematite to powder, mixed it with oil, grease, mucilage or gums and applied it as a heraldic decoration to his face or wigwam, or used it in the crude decoration of his household utensils.

The history of all races in the use of paint is practically the same. The first pigments used are the natural earth colors or simple vegetable dyes. They are devoted to personal decoration—commonly heraldic—and later their use is extended to other decorative purposes. It is only in a higher stage of development and civilization that the protective value of paint is recognized. This evolution is the natural accompaniment of change from the nomadic state, where dwellings are temporary, to the fixed life of civilized society.

Let us consider a typical high grade paint formula. It contains the following ingredients:

ANALYSIS OF PEA GREEN

(United States Standard Measure)

	Per cent.
Pigment by weight	48.00
Thinner by weight	52.00
	100.00
Thinner is composed of:	
Linseed oil	85.00
Asphaltum spirits	3.00
Turpentine	1.00
China wood oil	2.00
Japan dryer	9.00
	100.00
Composition of pigment:	
Basic carbonate white lead	15.00
Basic sulphate white lead	20.00
Zinc oxide	44.00
Magnesium silicate (asbestine)	3.00
Calcium carbonate	2.00
Barium sulphate (blanc fixe)	10.00
Aluminum silicate	3.00
Lead chromate	2.30
Ferric-ferro cyanide	.70
	100.00
Coloring is composed of:	
Pure chrome green	100.00
Composition of Japan dryer:	
Kauri gum	1.67
Oxide lead	8.45
Manganese peroxide (black oxide of manganese)	2.00
Linseed oil	26.44
Turpentine	61.44
	100.00

Let us also consider, in connection therewith, two other highly commended formulas—first the celebrated "Olive Drab" Cantonment paint of the United States Government and second, the very latest development in lithopone—zinc oxide formulas.

OLIVE DRAB PAINT

United States Army Standard W. D. 28

	Per cent.
Pigment	64
Liquid	36
White lead (basic carbonate, basic sulphate or a mixture thereof) not less than	42
Zinc oxide, not less than	33
The balance to consist of aluminum silicate, magnesium silicate or a mixture thereof, combined with the necessary pure tinting colors to produce the desired shade.	
Liquid	
Pure raw linseed oil, not less than	68
The balance to be combined drier and thinner. The thinner shall consist of turpentine or volatile neutral spirits or a mixture thereof.	

"40-40-20"

Pigment

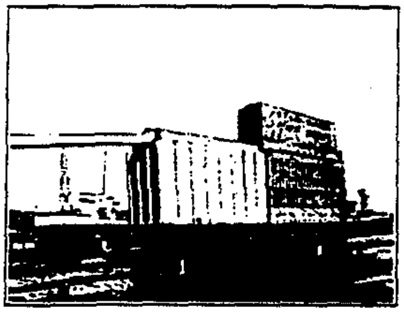
	Per cent.
Lithopone (light resistant)	40
Zinc oxide (lead free—Amer. proc.)	40
Asbestine	10
Silica	10
Liquid	
Boiled linseed oil	45
Raw linseed oil	40
Liquid drier	5
Turpentine	5
Heavy-bodied oil	5

Besides these ingredients that are mentioned in the formulas, we may also notice that the container is made of tin plate: that the can is soldered; that the labels are printed with two colors of printing ink on white paper, and pasted on the can. Finally we may recall that such cans are packed with sawdust in wooden boxes nailed together with steel wire

nails. Keeping in view the finished can and its contents, I think you will catch my drift when I say that all science and all civilization have gone to the making of cans of paint bearing these labels and that without science and civilization it would be unthinkable.

Linseed Oil—Ripe Flax

Let us consider briefly the ingredients, one by one: The first is linseed oil, a product of the flax plant, *Linum usitatissimum*. The flax plant was not first cultivated by man for the seed or its oil. Its earliest use was for the making of linen cloth. The great masters of early European art knew nothing of linseed oil, and the first use of the seed was medicinal. Today in the United States alone over thirty million bushels of flaxseed are consumed annually in the manufacture of linseed oil, the great bulk of which goes to the production of paint and varnish. To produce so much seed requires about three million acres of soil. Its cultivation requires many farmers and

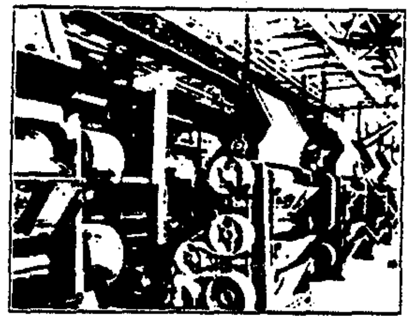


Linseed Oil—Seed Storage

laborers, much special machinery; its storage and transportation utilizes elevators, railroads, steamships; its use for oil-making requires elaborate plants, much special machinery; and the treatment of the oil for its various uses involves chemistry and the mechanical arts. Moreover, the oil-growing flax is itself a product of agricultural science, a science which is today more ardently pursued by plant spe-

cialists than ever before. The proper preparation and use of linseed oil involves the results of profound study and investigation, which today are still far from completion.

In the manufacture of linseed oil the flaxseed, cleaned from foreign seed and other im-



Linseed Oil—Crushing Rolls

purities, is first ground in a series of roller mills. The resultant meal is treated in a special heater with live steam to break up the oil cells. This hot meal is then pressed into the desired form and size for the oil presses, in a cake former; and a number of those cakes are stacked, one above the other, in camel's hair or other fabric cloths, between the plates of a specially devised hydraulic press. An

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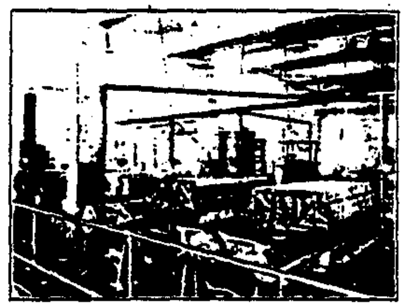
enormous pressure is applied and the expressed oil is filtered and collected in settling tanks, where the moisture, plant mucilage, etc., settle to the bottom, while the clear oil collects on top and is drawn off and sold as raw linseed oil.

Linseed Oil Presses, Etc.

Linseed oil is a very complex organic chemical compound, but consists essentially of the glycerides of a number of fatty acids. Of these the most important in connection with our subject are the glycerides of linolic and linoleic acids, to which the oil owes its characteristic property of absorbing oxygen and thereby becoming converted to linoxin—the

characteristic rubber-like product of "dried" linseed oil.

The presence of certain metals facilitates this process, and these metals are incorporated with the oil by heating their compounds with the raw oil. The three metals practically most



Linseed Oil—Filter Presses

effective for this purpose are lead, manganese, and cobalt, and consequently advanced manufacturers have generally abandoned the use of other compounds.

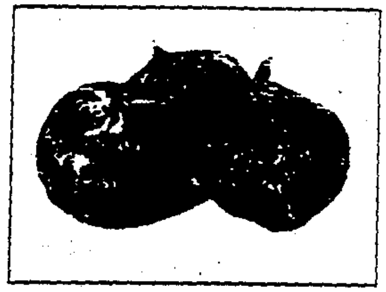
It will be noted that the liquid portion of our paints contains 85 per cent. of linseed oil. The fact is significant, for while linseed oil leaves something to be desired when we contemplate the ideal paint, it is nevertheless the most satisfactory paint oil for general use known to us up to the present time.

The remaining fixed oil in our first formula is China wood oil, of which only 2 per cent. is present. China wood oil is comparatively a recent addition to the raw materials of paint

Chinese Farm With Tung Trees

and varnish manufacture. It is expressed from a nut grown on a tree (*Aleurites Fordii*) indigenous to the Yangtze Valley, in China. The variety producing the oil nut is known to the Chinese as *ying tzu tung* (apple fruit Tung) and the tree is cultivated by the Chinese farmer for its oil. It grows to a height of about twenty-five feet, bears large green leaves, small pinkish flowers and large

green fruit somewhat resembling an apple. The seeds are large and poisonous, and from them the oil is obtained. The machinery used is primitive, consisting essentially of a wooden press operated by wedges. The oil is traded, along with other agricultural products, to mer-



Tung Oil—The Fruit.

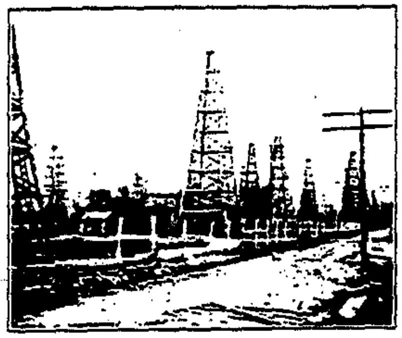
chants at Hankow, Fatchau and Canton. It has been used in China for ages, much for the same purposes as linseed oil is used in this country, and it is said that the extracted seed residues are the raw material for the manufacture of India ink.

The chemistry of this oil is still under investigation; but its "drying" properties are due, as in the case of all drying oils, to the presence of the glycerides of unsaturated fatty acids. It has drying properties similar to a certain extent to those of linseed oil, and the rate of hardening is accelerated by the same agencies that promote the oxidation of the more familiar oil. The chemical process appears, however, to differ, since while linseed oil hardens progressively from the surface inward, China wood oil seems to harden or set simultaneously throughout. This peculiarity led to rather expensive disasters in the earlier attempts to utilize the oil in this country. The drying salts are incorporated in practice at a comparatively low temperature; but in these earlier experiments the oil was treated at the temperature common in the treatment of linseed oil, with the result that the entire batch suddenly thickened to the consistency of rubber, in the kettle.

The discovery that rosin prevents this polymerization inaugurated a new era in the paint and varnish industry. China wood oil and rosin varnish are the principal vehicles of flat wall paints, of which there is a very large annual consumption; and in varnish making the same combination has to an important extent replaced fossil gums in the manufacture of high grade varnishes for many purposes. These gums are still used, but generally in combination with China wood oil and esterized rosin,—the so-called "ester gum," which is a chemical compound of rosin and glycerine.

The cultivation of the tung tree on a commercial scale was begun in 1923 at Gainesville, Fla., by the American Tung Oil Corporation, and this undertaking will eventually provide a portion at least of the quantity annually required. Oil from older American trees has proved superior to the imported product.

The two volatile ingredients of our formula are asphaltum spirits and turpentine. Asphaltum spirits is one of the lighter products of petroleums having an asphaltum base. It corresponds to the benzine which is produced from petroleums with a paraffin base. The chemistry of these hydrocarbons, while interesting, plays no part in the chemical structure of the paint film, since their office is purely mechanical and they disappear completely in the drying of the paint. As is well known, the petroleums found in some localities yield, in distillation at high temperatures, residues containing paraffin, while similar oils from other localities yield asphaltums as residues. The best known petroleums of the latter class are those produced in Texas, Oklahoma, California and the Island of Borneo. Petroleums are distilled by fractionating, the products passing over at the lower temperatures being classified progressively as petroleum ethers, naphthas and gasolenes, and benzines. The benzines having the higher "flash" points are known in the trade as "mineral spirits." At still higher temperatures the illuminating oils pass over, followed by the lubricating oils. Mineral spirit is usually a high boiling point benzine of the asphaltum petroleums. It boils at a higher temperature than the corresponding paraffin product, has a higher specific gravity and is, on several accounts, preferable as a volatile ingredient of paints. I personally believe that the formula before us is mechani-



Petroleum Industry—Oil Wells

cally improved by the presence of this material and I am convinced that it is in no way injured by it.

Turpentine is the essential oil of certain pines, principally *Pinus Australis*, growing over large areas of our Southern States. It is distilled in a current of live steam from the sap of this tree, the residue being rosin. The industry, owing to the character of the

labor available in the pine districts, is crude and wasteful both to the timber involved and to the product, though more conservative methods have come into use through the effort of the United States Department of Agriculture. This involves the substitution of

Turpentine Industry—Collecting and Shipping

porcelain pots for the archaic "box," and less injury to the tree.

The negro workman in a turpentine orchard cuts a so-called "box" on one side of the tree, in which the sap collects, and from which it is from time to time dipped and carried to the still. As the flow of sap decreases, the bark is removed and the wood sacrificed higher and higher above the "box." In the larger trees several boxes are cut at different points on the circumference, weakening and in time killing the tree. The crude sap or gum is charged into a still with water, and on heating, the volatile turpentine passes with the

Turpentine Industry—Improved Method of Collection

steam to the worm condenser. The turpentine is decanted from the condensed steam on which it floats.

Turpentine in paint probably acts in two ways: first, as a volatile thinner, of which the effect is purely mechanical; and secondly, as a conveyor of oxygen, perhaps catalytically. At any rate, it was the conclusion of a French technical commission who investigated the sub-

ject, that turpentine hastens the drying of paint to an extent not accounted for by its volatility.

The principal turpentine forests of today are located in Florida, southern Georgia and Louisiana, the immense forests that formerly covered vast areas in North and South Carolina and northern Georgia having been largely destroyed by the wasteful methods in vogue.

Another form of turpentine has appeared in the market during comparatively recent years. It is familiarly known as wood turpentine, being produced, by various methods of distillation, from pine wood wastes. When properly prepared by distillation in a current of steam and purified, there appears to be no practical difference in its properties as a paint vehicle from those of sap turpentine; and the product is more uniform.

The remaining liquid ingredient of our first formula is Japan dryer. This consists essentially of the linoleates of lead and manganese, with a small percentage of Kauri gum. It is prepared by boiling linseed oil with the proper percentages of compounds of manganese and of lead, adding thereto a certain quantity of melted Kauri gum, and reducing the product while warm, with turpentine, benzine or a mixture of the two. The lead compound used in this dryer is red lead and the manganese compound is the black oxide, while the reducing agent is turpentine and mineral spirit.

The manufacture of red lead leads us at once into the mining regions of the West,

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where in some districts lead is produced from practically pure ores, while in others it must be separated from its commingled silver, zinc, etc.

For the manufacture of the so-called Dutch Process white lead it is necessary to have the metal free from silver, manganese and iron; but for the manufacture of the oxides (red lead and litharge) purity is not so important. The metallic lead comes from the smelter in the form of pigs, which are melted in a low, flat oven in which the lead spreads out in a thin layer and is mechanically worked so as to expose continually fresh surfaces to the action of the air. The product is the monoxide of lead—massicot. This oxide is ground with water to remove metallic particles, which are returned to the furnace, while the oxide is collected in settling tanks. If the temperature in the furnace rises too high it becomes litharge—crystalline lead monoxide—which cannot be further oxidized.

The amorphous monoxide, being further treated in the same or a similar oven, at a low red heat, with free access of air and constant stirring, gradually takes up more oxygen and is converted into red lead—a combination of the monoxide and the dioxide, in the proportion of about two parts of the former to one of the latter. The product is usually stated as having the formula Pb_3O_4, but red lead produced in this way is, as noted, a mixture of oxides rather than a definite chemi-

cal compound. The product from mechanical furnaces, however, is almost completely oxidized to pure red lead.

The black oxide of manganese, known to mineralogists as Pyrolusite, is a natural product, of which the principal sources of supply

Red Lead Furnace

are in the Caucasus Mountains, in the Hartz Mountains in South America and elsewhere. Chemically, it is the dioxide of the metal manganese. The miners in the Caucasus are the wild mountaineers of eastern Europe, and the mineral, before it reaches America, passes through Southern Russia, the Black Sea, the Dardanelles, the Mediterranean and so across the Atlantic. For the use of the varnish and dryer manufacturer it is subjected to mechanical purification.

These two metallic oxides readily replace the glycerin in linseed oil at moderate temperatures, forming oleates and linoleates, while the glycerin is decomposed and driven off.

The addition of a resin—in this case Kauri

Manganese Mine in the Caucasus Mountains

gum—at a moderately high temperature also probably induces the formation of resin acid compounds of the metals.

The driers made with lead and with manganese have sharply distinguished properties, of which advantage is taken by the well-informed manufacturer who knows that certain proportions of the two yield better average results than either alone. He also carefully calculates the percentage of the metal in the drier to the oil to be oxidized. Kauri gum,

besides helping the quality of the japan, has also been shown by experience to serve a useful purpose in paints containing high percentages of zinc oxide. It is found only in New Zealand, where ancient forests of the tree which produced it—the *Dammara australis*

Kauri Tree—Dammara Australis

and other varieties of *Dammara*—have been buried for ages in the earth. It is mined systematically by trenching and is cleaned, sorted and classified by hand.

We have now briefly covered the liquid portion of our first formula and in the course of our survey have gone to North Dakota for

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flaxseed, to Florida for turpentine, to Texas for benzine, to China for wood oil, to Colorado and Montana for lead, to the Caucasus for manganese, and to New Zealand for Kauri gum.

Even at this point we may begin to see

Kauri Gum Diggers

that for this ordinary can of mixed paint the manufacturer has been under the necessity of calling upon many industries, several races and different quarters of the globe. It is no less so with the remaining items of our formula and the package in which it is sold. Lead hydrocarbonate is the first named of the solid ingredients. In this case it happens to be Dutch Process White Lead.

Lead hydrocarbonate or basic lead carbon-

ate is a molecular combination of the hydroxide and the carbonate of lead in about the proportion of two parts of the latter to one of the former, though these proportions are only approximated in actual practice. The accepted formula, however, is $2PbCO_3 . PbH_2O_2$.

Kauri Gum—Trenching

The Old Dutch Process, so called—though it has undergone great improvement in English and American practice—starts with desilvered lead pigs, known in the trade as "soft lead." These are melted, and the molten lead is distributed in shallow moulds on an endless chain belt. The moulds give the metal the form of a flat circular grating or buckle about 3/16 inch thick by 5 inches in diameter. These buckles are packed into earthenware pots, having at their bottoms shallow wells

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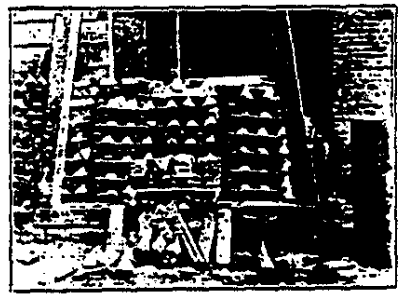
containing each about half a pint of vinegar or dilute acetic acid. The charged pots are arranged in tiers between layers of spent tan bark, where they are allowed to remain undisturbed for about 130 days. By the fermentation of the tan bark heat is generated and

Dutch Process White Lead—Corroding Pot

carbonic acid liberated. The heat vaporizes the acetic acid, which attacks the lead, coating the buckles with basic lead acetate. This in turn is attacked by the carbonic acid, producing the basic carbonate and liberating neutral lead acetate, which attacks the metallic lead beneath, producing again the basic acetate. The process thus continues progressively until

most of the buckle has been altered to the basic carbonate. The buckles being removed from the pots are subjected to mechanical treatment which separates the corroded from the uncorroded portions. The white lead after being ground, washed, floated and dried, enters com-



Dutch Process White Lead—"Pigs" and "Buckles"

merce as dry white lead. The special characteristics of corroded white lead are its excellent working properties and low oil consumption, giving a high degree of opacity or color-body in the finished paint.

The second process, commonly known as the "quick process," or "Carter process," also starts with desilverized pig lead. This is melted and finely comminuted in a steam blast, and the granulated product is charged into large, slowly revolving wooden drums, where, after being moistened with dilute acetic acid, it is subjected for some hours to the action of purified carbonic acid gas from burning coke. The slow revolution of the drums insures the exposure of the entire mass to the action of

Dutch Process White Lead—Melting Furnace and Chain Molds

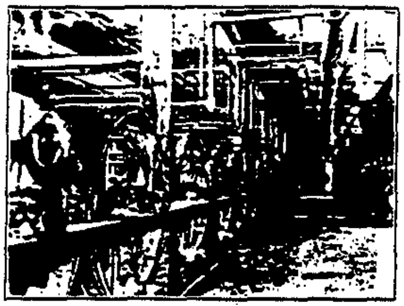
the gas. The chain of chemical processes involved is probably identical with those described for the Old Dutch Process. The mechanical treatment of the crude corroded product is essentially the same. The finished product is more uniform in the size of particle than Dutch Process Lead and finer in texture. This involves a larger oil consumption and a consequent decrease in opacity or color body of the completed paint.

The second pigment of our formula is

Basic Lead Sulphate or Basic Sulphate White Lead. This is a sublimation product, and is produced directly from the native ores of Missouri—lead sulphide—by oxidation at a high temperature in a current of air. The comminuted ore is charged in a special fur-

Dutch Process White Lead—Building "Stack"

nace with coal or other fuel and is subjected to a hot-air blast. The sulphide takes up oxygen, volatilizes and is carried through a series of cooling flues to fabric bags, in which it is collected. This is the process in outline, though not in detail. The reaction involved is simple; the lead sulphide, PbS, takes up four equivalents of oxygen from the air, being converted into lead sulphate, $PbSO_4$. At the same time it is also claimed, with much probability, that there is formed a certain proportion of the basic lead sulphate, $Pb_3S_2O_9$. At any rate analysis always yields an excess of oxygen, which is usually calculated to lead oxide, the percentage of which ranges from fourteen to twenty. The product, furthermore,



"Quick Process" White Lead—Corroding Drums

always contains a small percentage (five to ten) of zinc oxide, which comes from the zinc sulphide associated with the ores used. It may be said in passing that lead sulphate, chemically produced, is a very unsatisfactory pigment, exhibiting none of the characteristics of the sublimed white lead. The latter, on the other hand, is extremely useful, and in certain combinations has come to be regarded as almost indispensable. The particles of this pig-

ment are extremely fine and uniform, approaching the particles of zinc oxide in this respect. As a pigment, it stands between corroded white lead and zinc oxide in most of its characteristics. Paints made with it chalk more freely than paints made with the former, but

Basic Sulphate White Lead—A Furnace

on the other hand, they retain their color better, and do not "check" so freely. Proper combination with zinc oxide restrains the characteristic chalking, while the hardening peculiar to zinc is in turn restrained.

Our third pigment is zinc oxide. Zinc is peculiar in that it is the only metal in common use produced by distillation. It is vola-

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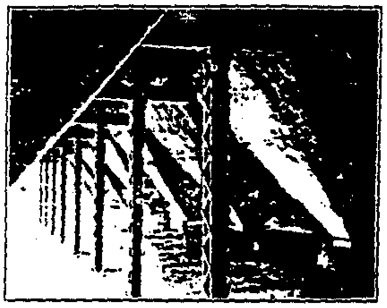
tile at an easily attainable temperature and advantage is taken of this fact in recovering the metal from its ores. The hot metallic vapor is also readily oxidizable, and if exposed to the air, will take fire, burning with a green flame to zinc oxide.



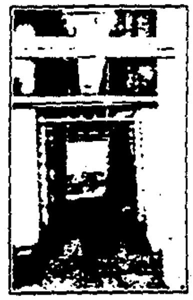
Basic Sulphate White Lead—Hoppers Under Collecting Bags

The oxide is produced by two different processes. One, known as the French Process, taking advantage of the fact just mentioned, volatilizes the metal in a current of air, and collects the resultant oxide in closed chambers.

In the other process, known as the American process, the oxide is produced directly from the ores. On the nature of the ore used

depend the individual characteristics of the resultant oxide.

In this process the finely granulated ores are mixed with powdered anthracite and charged into closed furnaces having perforated grate bars. Combustion is started in the anthra-



Zinc Oxide—Bag Room

cite and a blast of air is forced through the perforations in the grate. The heat smelts the ore and volatilizes the zinc, and the metallic vapors promptly combine with the oxygen of the blast, producing zinc oxide. This oxide is carried through a series of cooling flues and collected in fabric bags. The particular oxide used in this formula is made from New Jersey ore, and on that account is of some interest. This ore is unique in that it occurs in commercially available quantities, nowhere else in the world. It is known as Franklinite, and consists of the oxides of zinc, manganese and iron in molecular proportion—crystallizing as a true mineral. It is closely associated in the vein with other compounds of zinc—the an-

Zinc Oxide—Furnaces

hydrous silicate, the oxide, etc. A peculiarity of the product is that the oxide recovered is practically free from impurities, averaging over 99 per cent. pure oxide. The oxides produced from the ores mined in other localities usually contain from 5 to 35 per cent. of lead sulphate, due to the presence of lead sulphide in the vein.

The characteristics of zinc oxide are too well known to require extended comment. It

is the finest and, excepting the best grades of lithopone, whitest of all white pigments; is chemically quite stable, the only chemical change possible in practice being to the sulphide or to the carbonate, which is also white. It is bulky and hence carries a high percentage of oil in the finished paint; and finally, when properly used, it is very durable. One is fairly safe in saying that if Oxide of Zinc had not been introduced as a pigment, there would have been no prepared paint. It was produced as a commercially available pigment in answer to a demand that had been voiced in Europe from the closing years of the Eighteenth Century, to the time of its introduction about the middle of the Nineteenth. This demand for a non-poisonous white pigment finally received a satisfactory response from a contracting painter of Paris, Le Claire, who was also celebrated as a philanthropist and is known to this day as "the father of profit sharing." Practically every great chemist of Europe from Lavoisier to Faraday had his try at the problem.

Our next pigment is magnesium silicate in the form of asbestine. This product comes principally from Canada. Its usefulness in the paint formula depends entirely upon its physical form, which is acicular or rod-like. Its office in the paint firm has been compared to that of the hair in plaster or the rods in reinforced concrete. It is without special value either for opacity or protection, but aids in

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holding the materials in suspension and very probably also in resisting stresses in the dried paint film.

Our fifth solid ingredient is Calcium Carbonate—in this case a natural product from Missouri—a dolomitic crystalline rock, finely ground for the purpose. Calcium carbonate, as used in paint manufacture, comes to us in two forms. Whiting, Paris White, etc., are the pulverized and floated chalk supplied principally by the chalk cliffs around Dover, England,—the calcareous skeletons of innumerable diatoms that once populated the waters of an ocean covering that portion of the earth, ages before the advent of man; while the product used in this formula is from a similar geological source, but in succeeding epochs subjected to heat and pressure, which gave it a crystalline structure. As a rule, manufacturers in selecting from these two forms are governed by the conditions: if the remaining inert pigments are crystalline, Paris White is selected; if not, then the so-called mineral primer is preferred.

Either will neutralize any free acid in the paint, but the mineral primer will in addition give the "tooth" which is thought desirable in the manual work of painting. The only other crystalline pigment in our formula is the asbestine, so mineral primer rather than a form of chalk has been selected for this formula.

Barium Sulphate is the next pigment on our

list, and is used in the form of the chemical precipitate—blanc fixe. Personally, I should have preferred the natural crystalline form, barytes in this case, but that is a matter of detail. The sulphate of barium in the form of barytes is a natural, crystalline prod-

Barytes Mining—Missouri

uct, which retains its crystalline form, no matter how finely comminuted.

It is found associated with lead, zinc and other ores in most mineral regions. That used in the United States, however, comes principally from Missouri and the Alleghenies, Missouri furnishing the larger proportion. There its production is in the hands of farmers who collect and cart it to the railroads in the fall and winter, to be manufactured into pigment at St. Louis and neighboring points. In the Allegheny regions the mineral is procured by mining.

It is largely used in the manufacture of lithopone, which is a compound of barium sulphate and zinc sulphide.

Blanc fixe is produced by transforming the natural product into a soluble compound and precipitating it from dilute solution with sulphuric acid or a soluble sulphate. The product is chemically identical with barytes, but physically quite different, being very finely divided and amorphous.

Silicate of alumina is the next ingredient of our white base. Technically, it is a washed and floated China clay, naturally produced by the disintegration of certain feldspars, the soluble potassium and sodium salts having been washed away. The percentage here used is small, but it has a physical influence on the suspension of the other pigments, in the brushing qualities of the paint and on the quality of the paint film.

An important white pigment of our third formula is lithopone. The importance of this pigment to the industry may be estimated from the fact that the annual consumption has grown from less than 10,000 tons in 1906 to well over 100,000 tons in 1924. It is a compound of barium sulphate and zinc sulphide with a small percentage of zinc oxide in the proportion, roughly, of about 68 per cent. barium sulphate, 30 per cent. zinc sulphide and 2 per cent. zinc oxide. In the manufacturing

process, solutions of zinc sulphate and barium sulphide in chemically equivalent proportions, are brought together in a precipitating tank. By mutual exchange of acids double precipitation of zinc sulphide and barium sulphate results. The precipitate is thoroughly washed, dried and finally furnaced. This furnacing is responsible for the conversion of a small percentage of the zinc sulphide to zinc oxide. The product is finely ground, further washed and bolted.

Ordinary lithopone has the serious defect of darkening in direct sunlight, recovering its whiteness in the dark. Until within recent years its use was consequently confined to interior painting—flat wall paints and "mill-whites" for example. Improvement in manufacturing processes has, however, resulted in the production of light resistant lithopones, and the use of the pigment in exterior paints has followed very rapidly. The formula under consideration is perhaps the most highly approved of this type.

The remaining ingredients of our formula are the colors required to produce the desired tint. They have no influence on the quality of the paint. The yellow in this combination is lead chromate—chrome yellow. It is produced by the reaction of a soluble chromium salt, usually sodium bichromate, on a soluble lead salt, usually lead nitrate, both in solution. The neutral chromate of lead, $PbCrO_4$, being insoluble, is precipitated. The produc-

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tion of this familiar pigment takes us far afield. The chromium used in making the chromates is obtained from an ore of iron known as chromite. It is a chromate of iron, having the composition $FeCr_2O_4$. It is found in small quantities in Pennsylvania, Maryland, California and elsewhere in the United States, but the main sources of supply are Asia Minor and New Zealand. Large quantities of these ores are imported into England, Germany and the United States for the sole purpose of manufacturing the chromium salts of potassium and sodium. The process is intricate and difficult, so that the manufacturers are few in number. There is also some demand for the mineral in the manufacture of special steels.

The remaining pigment is Prussian Blue—the potassio-ferro-ferri-cyanide of iron. This material brings us once more into the field of organic chemistry, the non-metallic component of the blue being cyanogen, which is most familiarly known as a component of hydrocyanic or prussic acid and the cyanides of potassium, etc. The chemical composition of the color is indicated by the formula $K_2Fe_22Fe\text{-}C_6N_6$.

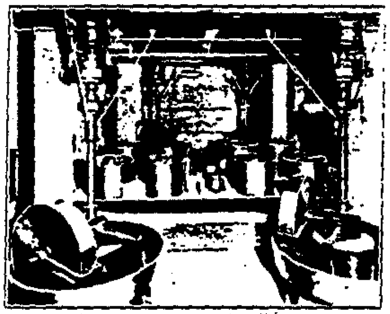
The cyanides are obtained from animal wastes containing carbon and nitrogen, such as waste liquors from gas works, dried blood, leather paring, hoofs, horns, etc. These are calcined with an alkali and the ash lixivated with water, and from this liquor cyanides of the alkali metal can be recovered, or the blue

may be directly obtained by precipitating with ferrous sulphate (copperas). In practice, in the manufacture of chrome green as used for tinting in the present instance, the colors are precipitated simultaneously from solution, either with or on the base, which in this case is the blanc fixe shown in the formula.

We have now glanced hastily at the characteristics of our several ingredients, but they are still only raw materials and require a long series of mechanical operations before our can of paint will be ready for use, not to mention the detailed work of the chemist to determine the quality of the materials themselves.

A modern paint factory is a complicated institution, and in the limits of such a paper as this can be touched upon only briefly and hastily. Power in the most modern plants is generated at a central point and is distributed to the units in the form of electrical energy. As a rule, the raw materials are elevated to the highest point in the plant, so that the product, in its several steps towards completion, may fall by gravity from each point to the next in the process.

The dry pigments are ground separately to the form of a paste with linseed oil. The various components of the white base are then thoroughly incorporated with more oil, the whole is then mixed with the rest of the oil and the remaining thinners in a mechanical agitator, the tinting colors being added either here or at the preceding step, and the exact tint is attained by addition on the judgment of the expert tinter. The finished paint is measured mechanically into tin cans, which are also soldered and labelled by machinery, and finally these cans are packed in cases holding a

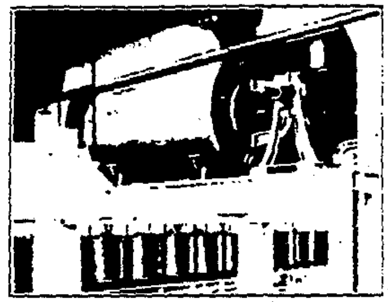


Paint Manufacture—Chasers and Mixers

given number and guarded from injury by sawdust, placed between them. The boxes are then nailed shut, marked and shipped to the distributors. This is the mechanical routine in the barest outline; but we may observe that it involves the use of building materials, fuel, copper wire, tinplate, paper, printing-ink, paste, box lumber, sawdust, wire nails, etc.

The manufacture of tinplate is an important industry in itself, involving a branch of the

steel industry in the production of the plates for this use. These plates are cleaned by chemical means, heated, and coated with metallic tin by dipping in a bath of the molten metal. To obtain the tin for this use we must again go to distant regions. Tin ores are found in



Paint Manufacture—Tank and Mixers

small quantities in various parts of the United States. I have in my own collection interesting specimens from South Dakota, West Virginia and Alaska; but so far no commercially available quantities have been found in these localities.

Cornwall, from the time when the Phoenicians traded to Britain for tin to the days of the first McKinley tariff, was the chief source of the world's tin supply. But the drain finally told on the natural resources, and the bulk of the tin consumed today comes from the Straits of Malacca and from Australasia. In the former locality it is recovered by placer mining methods and in the latter by the usual methods of underground mining. The ore is found in two forms, as the oxide, Cassiterite, and as the sulphide, Stannite, in which latter form it is associated with iron. The smelting of the ore for the metal is done principally in England and other parts of Europe.

The paper for our label is a product of sulphite wood pulp, as is most of the paper used for advertising paint. We need not enter farther into this subject except to note that our industry involves also the paper manufacturing industry.

Similarly we may note in passing that the printing ink manufacturer and through him the lamp black manufacturer, the color maker and the varnish manufacturer are involved.

Finally, in the consumption of paste, we return once more to the farmer, on whom we called in the first instance for our linseed oil. In order that I may not be suspected of straining for effect when I include these items in the enumeration, it will be interesting to know that in the year 1909 one paint manufacturer reports to me the following items:

Paper for labels	$2,520.00
Paper for advertising matter..............	18,840.00
Black and colored ink for labels and advertising matter	2,736.00
Solder for soldering tin cans (of which again tin is a constituent), pounds............	125,227
Output of colored samples, pieces..........	33,236,342

For 1924 these figures should all be increased by about 60 per cent.

Appendix

Flaxseed, Including Linseed Oil

Production, imports, exports and net supply in the United States, 1911-1922. Compilation by United States Department of Agriculture, 1923

Year Beginning July 1	Production Bushels	Imports of Seed Bushels	Imports of Oil* Bushels	Exports of Seed (Domestic and Foreign) Bushels	Exports of Oil (Domestic and Foreign)* Bushels	Net Supply Bushels
1911-12	19,370,000	6,841,806	204,902	26,242	99,085	26,381,381
1912-13	28,073,000	5,294,296	69,476	17,062	693,579	32,726,131
1913-14	17,853,000	8,653,235	76,116	305,596	95,775	26,181,577
1914-15	13,749,000	10,666,215	214,116	67,173	481,857	24,077,301
1915-16	14,030,000	14,679,233	20,039	2,031	285,648	28,441,013
1916-17	14,296,000	12,393,958	44,423	1,017	480,622	26,252,672
1917-18	9,164,000	13,366,529	20,131	22,342	476,216	22,052,312
1918-19	13,369,000	8,426,896	393,923	15,618	439,173	21,737,020
1919-20	7,256,000	23,391,934	1,820,156	48,980	456,806	31,962,304
1920-21	10,774,000	16,170,415	798,634	1,496	224,514	27,517,049
1921-22	8,029,000	13,632,073	8,997,620	2,281	148,605	30,507,807
1922-23	10,375,000	25,005,936	3,027,399	121†	165,605	38,242,314

Division of Statistical and Historical Research. Compiled from reports of the Bureau of Foreign and Domestic Commerce and Division of Crop and Live Stock Estimates.

* Stated as seed equivalent, 2½ gallons of oil equal 1 bushel of seed.

† Six months beginning July 1, not separately reported in 1923.

Note—The estimated United States production for 1921 was 10,672,000 bushels; total of the world, 132,867,000 bushels. The "net supply" (United States) for 1922-1923 was the equivalent of 95,606,285 gallons of linseed oil.

The United States Census of Manufacturers reports the following figures on paint and varnish production for the calendar year 1923:

Paints and Varnishes

The establishments engaged primarily in the manufacture of paints and varnishes reported products valued at $404,134,231, an increase of 47.3 per cent. as compared with 1921, the last preceding census year. For the paint industry alone the total value of products reported was $291,123,738, an increase of 43.4 per cent. as compared with 1921; and for the varnish industry alone, $113,010,493, an increase of 58.6 per cent.

For the major groups of products (including paints and varnishes manufactured as subsidiary products by establishments engaged primarily in other industries), the statistics show the output for 1923 and the rates of increase as compared with 1921, as follows: Colors (pigments)—value, $88,446,196, an increase of 85.7 per cent. Paints in-oil in paste form—value, $48,731,938, 4.6 per cent. Paints in oil, ready mixed—quantity 69,628,976 gallons, 44.8 per cent.; value, $123,547,880, 35.6 per cent. Water paints and kalsomines—value, $9,141,865, 104 per cent. Varnishes and japans—value, $118,183,673, 66.1 per cent.

Of the 826 establishments reporting for 1923, 132 were located in New York, 100 in Pennsylvania, 90 each in Illinois and Ohio, 70 in New Jersey, 57 in California, 37 in Missouri, 34 in Massachusetts, 24 in Michigan, 23 in Indiana, 22 in Maryland, 21 in Kentucky, 17 in Minnesota, and the remaining 109 in twenty-three other states and the District of Columbia.

The statistics for 1923 and 1921 are presented in the following tables. The figures for 1923 are preliminary and subject to such correction

as may be found necessary upon further examination of the returns.

Table 1—General Statistics for the Industries, 1923 and 1921

Paints

	1923	1921	Per cent. of Increase
Number of establishments	602	582	3.4
Wage earners (average number)*	17,18[illegible]	13,877	23.8
Maximum month	Apr. 18,217	May 14,681	...
Minimum month	Dec. 16,295	Aug. 13,249	...
Per cent. of maximum	89.4	90.2	...
Wages	$21,830,231	$17,431,917	25.2
Cost of materials (including fuel and containers)	$184,206,126	$127,263,8[illegible]	44.7
Products, total value	$291,123,738	$203,071,1[illegible]	43.4
Value added by manufacture†	$106,917,612	$75,807,2[illegible]	41.0
Horsepower	94,05[illegible]	‡	...
Coal consumed (tons of 2000 lbs.)	577,473	‡	...

Varnishes

	1923	1921	Per cent. of Increase
Number of establishments	224	222	0.9
Wage earners (average number)*	5,636	4,138	36.2
Maximum month	Apr. 5,966	May 4,366	...
Minimum month	Jan. 5,434	Feb. 3,954	...
Per cent. of maximum	92.0	89.0	...
Wages	$8,040,944	$5,861,36[illegible]	37.2
Cost of materials (including fuel and containers)	$64,748,566	$44,133,[illegible]	46.7
Products, total value	$113,010,493	$71,239,18[illegible]	58.6
Value added by manufacture†	$48,261,927	$27,105,200	78.1
Horsepower	21,134	‡	...
Coal consumed (tons of 2000 lbs.)	83,962	‡	...

* Not including salaried officers and employees nor proprietors and firm members. Statistics for these classes will be given in final report.

† Value of products less cost of materials.

‡ Not reported.

Table 2—Detailed Statistics of Products, 1923 and 1921

	1923	1921
Total value	$432,873,070	$258,497,118
The paint industry	$291,123,738	$203,071,131
The varnish industry	$113,010,493	$71,239,153
Subsidiary products of other industries	$28,738,539	$14,386,804
Colors (pigments) ...value	$88,446,196	$47,637,057
White lead, dry ..pounds	317,136,109	334,948,764
For sale ....pounds	156,179,967	123,867,530
value	$11,934,339	9,071,518
Made and consumed, pounds	160,956,142	211,081,234
Lead oxides......pounds	219,429,751	139,814,627
For sale.......pounds	209,613,316	129,637,108
value	$20,199,300	$9,323,019
Made and consumed, pounds	9,816,465	10,177,519
Lithopone ....pounds	201,154,430	96,983,984
For sale.......pounds	200,910,621	96,434,572
value	$12,445,090	$6,118,907
Made and consumed, pounds	243,809	549,412
Zinc oxide.......pounds	309,669,368	117,127,315
value	$22,472,299	$1,951,887
Iron oxides......pounds	126,908,010	85,128,358
value	$3,133,953	$1,951,887
Chrome yellow, orange, or green**.......pounds	26,316,569	13,429,231
value	$4,671,091	$2,379,126
Prussian blue....pounds	3,137,777	1,668,004
value	$1,464,645	$851,835
Other colors*......value	$12,134,998	$8,711,677
Paints in oil.........value	$172,299,818	$137,695,634
In paste form, ground in oil ....value	$48,751,938	$46,603,452
White lead....pounds	272,491,375	329,668,229
value	$30,323,436	$32,685,937
Zinc oxide.....pounds	7,881,428	7,227,587
value	$959,764	$803,155
Other, in paste, pounds	126,867,216	91,260,293
value	$17,468,688	$13,114,340
In oil, ready mixed ......gallons	69,628,976	48,068,183
value	$123,547,880	$91,092,182
White paints and kalsomines ....value	$9,141,865	$4,482,329
Dry or in paste...pounds	122,217,347	87,744,675
value	$3,334,187	$4,394,959
Mixed for use...gallons	1,727,116	31,330
value	$3,607,678	$87,370

Varnishes and japans, value	$118,183,673	$71,136,904
Oleoresinous varnishes, gallons	39,378,453	22,172,143
value	$51,402,630	$29,033,763
Spirit varnishes, not turpentine .....gallons	5,605,568	3,084,507
value	$10,584,374	$7,255,260
Damar and similar turpentine and benzine varnishes ....gallons	3,862,643	4,293,923
value	$6,143,519	$6,167,731
Pyroxylin lacquers and enamels ....gallons	2,333,474	1,409,280
value	$3,094,210	$3,093,862
Drying japans and dryers, gallons	7,329,264	4,313,329
value	$6,719,722	$3,669,335
Baking japans....gallons	6,470,773	3,464,625
value	$6,196,746	$4,245,182
Enamels ....gallons	13,381,889	6,384,375
value	$27,329,425	$14,737,302
Other products of the varnish group—asphaltums, varnish stains, etc.....value	$4,512,997	$2,275,249
Fillers, liquid, paste, and dry ....value	$2,981,110	$2,649,036
Putty ....pounds	90,249,365	65,897,542
value	$3,674,459	$2,641,831
Other affiliated products, value	$16,381,443	$11,092,243
All other products....value	$21,364,504	$11,362,083

*Barytes, ultramarine, vermilion, other mineral colors, dry colors, fine colors, coal-tar color lakes, and pulp colors sold moist.

The United States Census of Manufacturers for 1923 gives the following statistics for rosin and turpentine:

Turpentine and Rosin

The establishments engaged primarily in the manufacture of turpentine and rosin from crude gum reported products valued at $35,166,715 for the crop year ended March 31, 1924. This represents an increase of 50.9 per cent. as compared with $23,300,845 for the year ended March 31, 1923, the last preceding biennial census year.

Of the 1203 establishments reporting for 1923-

1924, 540 were located in Georgia, 429 in Florida, 131 in Alabama, and the remaining 103 in Louisiana, Mississippi, North Carolina, South Carolina and Texas.

The total production of turpentine by all classes of establishments increased from 24,820,620 gallons during the crop year 1921-1922 to 29,781,944 gallons during the crop year 1923-1924, the rate of increase being 20 per cent., and the output of rosin increased during the same period from 1,690,971 barrels to 1,990,865 barrels, the rate being 17.7 per cent.

Although turpentine and rosin are produced principally from crude gum, considerable quantities are made by the distillation of wool, by both the steam and destructive processes. During the calendar year 1923, 2,607,364 gallons of turpentine and 200,778 barrels of rosin were produced by this method. These quantities represent increases of 490.2 per cent. and 584.2 per cent., respectively, as compared with the calendar year 1921.

General and special statistics are presented in the following tables. The figures for the calendar year 1923 and for the crop year 1923-1924 are preliminary and subject to such correction as may be found necessary upon further examination of the returns.

Table 1—General Statistics for Establishments Using Crude-Gum Distillation Method, Crop Years Ended March 31, 1924 and 1922

(No data included for establishments with products under $5,000 in value.)

	1923-1924	1921-22	P. C. of increase
Number of establishments	1,203	1,062	13.3
Wage earners (average number)*	34,328	27,422	25.2
Maximum month	Sept. 35,077	Aug. 28,370	....
Minimum month	Jan. 33,126	Feb. 26,450	....

Per cent of maximum	94.4	93.2	....
Wages	$15,448,590	$9,512,177	62.4
Cost of materials (including fuel and containers)	$8,972,738	$6,199,179	44.7
Products, total value	$35,166,715	$23,300,845	50.9
Value added by manufacture†	$26,193,957	$17,101,666	53.2
Horsepower	1,942	(c)	....

*Not including salaried officers and employees, nor proprietors and firm members. Statistics for these classes will be given in final report.

†Value of products less cost of materials.

(c)—Not reported.

Table 2—Total Production of Turpentine and Rosin From Crude Gum and Wood, Crop Years Ended March 31, 1924 and 1922*

(Includes data for establishments with products valued at less than $5,000.)

	1923-24	1921-22	P. C. of increase
Turpentine, total:			
Quantity (gallons)	29,781,944	24,820,620	20.0
Value	$23,326,702	$13,590,002	86.4
Rosin, total:			
Quantity (barrels, 500 lbs.)	1,990,865	1,690,971	17.7
Value	$13,392,043	$10,996,358	21.8
Distilled from crude gum:			
Turpentine—			
Quantity (gallons)	27,174,580	24,378,854	11.5
Value	$23,312,036	$13,356,790	74.5
Rosin—			
Quantity (barrels, 500 lbs.)	1,790,087	1,661,624	7.7
Value	$12,023,958	$10,796,975	11.4
Distilled from wood:†			
Turpentine—			
Quantity (gallons)	2,607,364	441,766	490.2
Value	$2,014,666	$233,212	763.9
Rosin—			
Quantity (barrels, 500 lbs.)	200,778	29,347	584.2
Value	$1,368,085	$199,383	586.2

Table 3—Stocks of Turpentine and Rosin on Hand March 31, 1924, and March 31, 1923

	March 31, 1924		March 31, 1923	
	Turpentine (gallons)	Rosin (barrels, 500 lbs.)	Turpentine (gallons)	Rosin (barrels, 500 lbs.)
Total	5,326,581	1,011,784	3,582,768	1,132,505
At stills	1,122,051	345,214	609,679	474,829

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In hands of consumers‡ .	934,530	264,558	833,477	297,843
At wood-distillation plants§	‖475,000	‖50,000	299,712	25,063
At ports and distributing points§	2,794,950	351,976	1,839,900	334,770

* Total production for crop year ended March 31, 1923: Turpentine, 24,252,835 gallons; rosin, 1,651,795 barrels.

† Statistics relate to calendar years 1923 and 1921.

‡ Produced by destructive process, 402,249 gallons; by steam process, 2,205,115 gallons.

§ Compiled by Bureau of Chemistry.

‖ Estimated.

It would probably be conservative to estimate the capital employed, more or less directly, in the paint and varnish industry at upwards of $550,000,000.