

UNITED STATES PATENT OFFICE.

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PROCESS OF MAKING ANTICORROSIVE PAINTS AND THE LIKE.

1,145,186.

Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that I, RUDOLF EBERHARD, citizen of Germany, residing at Munich, Bavaria, Germany, have invented certain new and useful Improvements in Processes of Making Anticorrosive Paints and the like; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to a method of manufacturing paints, thinners, paint mixtures and vehicles for paints; all of said means being especially adapted to prevent the formation of rust.

It is an object of the invention to combine oils and fats, or the products derived therefrom, like wax, resins, and the like with certain compounds of chromium in order to obtain a product which readily adheres to iron and which has approximately the same coefficients of expansion as iron, so that changes in the dimensions of the metal, caused by fluctuations of temperature are also accompanied by similar changes in the dimensions of the coat of paint or the like.

Another object of the invention is to provide a coating which is impermeable and which protects the iron against injurious influences of the atmosphere, water and the like.

Another object of the invention is to utilize in the combination with oils, fats, and the like, compounds of chromium which contain the radical "chromyl", said chromyl compounds being preferably adapted to modify the consistency of the end product to the desired extent.

Another object of the invention is to utilize compounds of alkali salts, or metals which are soluble in ether, alcohol, or the like. This combination has the advantage that the final product is not injuriously influenced by the action of oxygen, carbon dioxide, or the like.

Another object of the invention is to combine the compounds of chromium mentioned above with the oils by a reaction of said compounds on chlorids of various metals.

Another object of the invention is to free the compound of the chlorin which may be developed during the reaction.

Other objects of the invention will be

more apparent by reference to the following specification and to the claims appended to the specification.

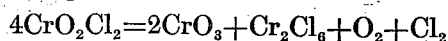
In the manufacture of chemically indifferent thinners and paints—and especially of rust preventing means—the pigment and vehicle must not only be adapted to withstand the damaging and decomposing actions from without, but these materials should also be preferably combined chemically. The material used as pigment should have in addition such qualities, as to place the same next to iron in the electro-chemical series.

If linseed oil or oil varnish respectively is used as a vehicle, linoxyn is formed gradually and the coat of paint superficially combined with the iron is rendered brittle and finally cracks on account of the different coefficients of expansion for iron and paint. The surface of the coat of paint which originally is impermeable renders possible the detrimental action of air, gas, water, etc., and rust sets in underneath the coat of paint. Another disadvantage of the paints in general use is the fact that an entirely homogeneous mixture of pigment and vehicle is never obtained and the formation of oil blisters cannot be avoided. This avoidance of free oil spaces is of great importance for means to prevent the formation of rust.

In order to eliminate the brittleness of anticorrosive paints the linseed oil or varnish was heretofore mixed with mineral oils, turpentine oil, gum, residues of the distillation of petroleum or similar materials, but all of these additions did not meet this purpose; and even the substitution of the above mentioned products in place of linseed oil or varnish did not prove satisfactory. An anticorrosive paint consisting of pigment and vehicle shall be of such qualities as to make it flow like a homogeneous liquid, which does not separate out into its components. A relatively favorable result is obtained by painting with white-lead or red lead since these materials partly combine chemically with the linoleic acid ($C_{18}H_{32}O_2$), but even these coats of paint do not offer sufficient protection and do not prevent the formation of rust; they were not more useful than the coats of paint applied with linseed oil or varnish without the addition of pigment.

It does not matter whether the varnish is obtained by boiling the linseed oil with compounds of manganese, lead, oxid, and the like, or whether it is obtained by any other method. Furthermore it has been shown that alkalidi-chromate and chromic chlorid retard the oxidation of iron; the utilization of the compounds of chromium for this purpose has been impossible up to the present time, owing to the fact that these compounds dissolve in water. It has also been attempted to use solutions of chromic oxid, resins, and chromic oxid linoleinates. These metal soaps and siccatives furnish only superficially binding, brittle coats of paints which do not expand with the iron, but they crack, drop off and can readily be removed. The addition of these substances to oil does not cause a change of the latter and these mixtures still have all the disadvantages of the coats of oil. The oils become thick by the mechanical dissolution of metallic soap, so that when applied to iron the disadvantageous oil spaces or blisters are formed in great numbers. The utilization of these products as a rust preventive means renders it also impossible to retain the natural color of iron.

The present invention is based on the fact that certain compounds of chromium soluble in oil or fat respectively, possess very valuable qualities for prevention of rust. These compounds have the same degree of oxidation as chromic acid, or an ethereal solution of chromic acid as well as of perchromic acid and also chromium phosphate dissolved in oil or fat. If linseed oil or varnish is acted upon in a suitable manner by chromyl chlorid, and if a violent reaction is prevented, a clear viscid greenish purple oil, or a varnish respectively is obtained which proves to be highly valuable as a rust preventing means. To prevent an excessive action of chromyl chlorid upon oils, varnishes, and the like, toluene nitro-benzene, chloroform, anilin or similar hydrocarbons as well as bisulphid of carbon may be used. The trichromyl chlorid freed when chromyl-chlorid is stored whereby simultaneously chlorin is formed may be used in the same manner as chromyl-chlorid (CrO_2Cl_2). It may be assumed that chromyl chlorid has also an oxidizing effect upon the oil—tending to convert it into a varnish—as well as a chlorinating effect, and that in thus acting it becomes decomposed according to the formula:



For certain purposes free chlorin or free chlorin compounds are harmful and therefore must be removed in the usual way, as for instance by absorption in water.

Instead of being treated with chromyl chlorid and trichromyl chlorid, oils, fats

and the like may also be treated with ethereal solutions of alkaline salts of chlorochromic acid (derived for instance from potassium dichromate and hydrochloric acid, or from chromyl chlorid and potassium chromate) to obtain the advantageous results mentioned above. The oil solution has a brown color at the beginning, and changes to green approximately within twelve hours. Furthermore chromyl fluorid and chromylacetate, as well as compounds of chromium in general, having the radical "chromyl", are suitable for the described purpose. Moreover a product may be used which is obtained by the action of chromyl chlorid upon sub-oxid of chromium. The reaction takes place under development of heat. The product has a viscous consistency, hardens when heated and becomes viscid when exposed to air; it is partly soluble in ether with a brownish color, which gradually passes into green. The part of the product of the reaction which is not soluble in ether, dissolves in alcohol, assuming a brownish color; the solution turns green during the state of rest. After this alcohol solution is mixed with a corresponding amount of ether it can be also mixed with oil. The original brownish color gradually passes into green. Additional tests have disclosed that the efficiency of these oil compounds of chromium as rust preventing means, increases in proportion to the per cent. of compounds of chromium therein. This effect is attained for instance, by dissolving chromic acid in ether, (whereby an ignition advisably is prevented by adding a few drops of oil to the ether) or by dissolving chrome phosphate in a suitable volume of oil, and by additional treatment of this solution with chromyl-chlorid or the like, as described above. Furthermore this increased effect may still be enhanced by using chlorinated and phosphureted oils, instead of common oils since they possess a greater dissolving power for the corresponding compounds of chromium. Thus only 0.1% of protochrome dissolves in ordinary oil, but 0.5% dissolve in chlorinated oil and 0.4% in phosphureted oil. Chromic anhydrid practically does not dissolve at all in ordinary oil without using ether as dissolving agent, but 0.5% of the anhydrid is dissolved in chlorinated oil and 0.4% in phosphureted oil. These solutions in their turn may be mixed together and may again be treated with chromyl chlorid.

Another method of utilizing compounds of chromium containing a chromyl radical and being soluble in oils and fats, consists of heating these compounds to a high temperature after they are dissolved in volatile solvents, as bisulfid of carbon, toluene, anilin, and the like; or of slightly heating these solvents in a tray until, for instance in using chromyl-chlorid, a brownish, oily liquid is

obtained. This liquid is a mixture of chromic anhydrid and anhydrous chromic chlorid, and it can be dissolved directly in oil thus avoiding the necessity of using a means to prevent violent reaction. A high percentage of suitable compounds of chromium dissolved in oil may be obtained in this way. If these compounds of chromium are dissolved in ether for instance, and applied to iron (without the use of oil or the like) a metallic lustrous precipitation is obtained on the iron after the ether evaporates, and this precipitation protects the iron against rusting. This shows conclusively that the compounds of chromium act chemically upon iron. It has furthermore been found advantageous to mix such compounds of alkaline earths and metals with the oil compounds of chromium which dissolve in ether or a mixture of ether and alcohol, or in bisulfid of carbon, or in similar solvents. These compounds also dissolve in oil, or by heating with oil dissolve in the latter without their chemical composition being changed by oxygen and carbon dioxide, and which are not used for making silver soaps or siccatives. In this class are for instance, perchlorid of manganese, permanganic acid, potassium permanganate, arsenic oxid, or arsenite of chromium respectively, arsenic acid, or chromearsenate respectively, the anhydrid of antimonie acid, antimony pentachlorid, the anhydrid of stannic acid, tetrachlorid of tin, mercury chlorid, lead tetrachlorid, cupric chlorid, calcium chlorid, strontium chlorid. The solution of arsenic oxid in oil is known, but the solution of arsenite of chromium in oil is novel and the solution of the arsenic oxid in oil in connection with the described oil compound of chromium is also novel. Cupric chlorid, calcium chlorid and strontium chlorid dissolve for instance in alcohol and by mixing the corresponding quantity of ether with oil, they may readily be dissolved.

It may be added that the above mentioned compounds of alkaline earths and metals may be used to obtain oil compounds and the like, without using chrome compounds. Furthermore compounds may be obtained soluble in ether or oil, respectively, which increase considerably the effect of the mentioned oil chrome compounds by causing chromyl chlorid (CrO_2Cl_2) to act upon the following compounds: anhydrid of manganese chlorid, bichlorid of manganese, antimony trichlorid, antimony pentachlorid, stannous chlorid, sodium stannate, tetrachlorid of tin, mercurous oxid, mercurous chlorid, mercuric chlorid, mercuric oxid, zinc oxid, zinc-chlorid, zinc carbonate, cuprous chlorid. For instance: 2.2 gr. antimony trichlorid with 1.6 chromyl chlorid were heated in a tray at the end of the reaction a greenish mass was obtained, which was dis-

solved in ether and mixed with 30 gr. of oil; the ether was again recovered by distillation.

Another reaction is the following: 2.1 gr. mercuric oxid acts upon 4.5 gr. chromyl chlorid at normal temperature; the reaction took place at once under considerable foaming; after settling the excessive chromyl chlorid (diluted with carbon bisulfid) has been removed and the residue was washed out with ether and this ethereal solution was mixed with 30 gr. of oil a brown solution was obtained. In the ethereal solution mercury compound and chromium were found.

Instead of chromyl chlorid, chromyl acetate or chromyl fluorid may be used to obtain corresponding compounds, or chlorochromate of alkali or chromic anhydrid and the like may be used. For instance: 2.3 gr. mercurous chlorid and 1 gr. chromic anhydrid, are at first slightly heated, whereby the mixture will show a red color and becomes moist. After continued heating a black powder is obtained which is treated with ether. The ethereal solution is mixed with 20 gr. of oil and the ether recovered by distillation. In the ethereal solution mercury compounds and chrome were found.

Examples.

(1.) 20 gr. stearic acid are diluted with 20 gr. carbon bisulfid and then mixed with 1 gr. chromyl chlorid, which was diluted with 10 gr. carbon bisulfid. Chromyl chlorid is added gradually while stirring the solution. From this solution the carbon bisulfid can be recovered by distillation. This preparation is a dark green liquid.

(2.) 20 gr. woolfat are dissolved in 20 gr. toluene and then mixed with 1.5 gr. chromyl chlorid which also is dissolved in 20 gr. toluene, and as indicated in Example 1 subjected to further treatment. This preparation possesses a brownish green color and is of a more solid consistency than the original woolfat.

(3.) 20 gr. paraffin (liquid) are mixed with 1 gr. chromyl chlorid which is dissolved in 10 gr. anilin. This solution shows at first a red color which gradually passes over to greenish brown.

(4.) 25 gr. linseed oil are dissolved in 20 gr. carbon bisulfid and mixed with 1 gr. chromyl chlorid which is dissolved in 10 gr. carbon bisulfid; and then subjected to further treatment as sub. 1. This preparation shows a greenish brown color.

(5.) 20 gr. yellow bees wax are dissolved in 20 gr. turpentine oil and diluted with 20 gr. toluene, then mixed with 1 gr. chromyl chlorid which is dissolved in 20 gr. carbon bisulfid, and subjected to further treatment as described. This preparation shows a dark green color and still has the smell of the wax and of the turpentine oil.

(6.) 15 gr. coal tar, mixed with .5 gr. chromyl chlorid are dissolved in 10 gr. carbon bisulfid and the latter recovered by distillation. The tar shows a blue black color, while the raw tar is brown black; and appears brown in thin layers. This preparation is more compact and possesses a greater covering capacity. A coat of paint dries and hardens in half the time than when ordinary tar is used, it is more elastic and no tears of tar are observed. Due to the greater covering capacity of the material its usefulness is increased; the disagreeable odor diminished considerably. The unsaturated compounds in the tar seem to be saturated since the coat of paint does not "creep". The mentioned qualities may still be enhanced by adding a higher percentage of chromyl chlorid, as indicated in the following example.

(7.) 30 gr. coal tar are mixed directly (without any agency) with 3.5 gr. chromyl chlorid. The tar assumes a higher temperature, giving off weak vapors.

(8.) 30 gr. fish-oil residues diluted in 20 gr. carbon bisulfid are mixed with .4 gr. chromyl chlorid dissolved in 5 gr. carbon bisulfid, whereby the latter is recovered again by distillation. The mixture is heated to 120° C. The substance loses practically all of its disagreeable odor.

(9.) 30 gr. naphtha residues are mixed with 1 gr. chromyl chlorid dissolved in 20 gr. carbon bisulfid and subjected to a corresponding additional treatment. The preparation is almost entirely without odor.

(10.) 30 gr. crude oil are mixed with 1 gr. chromyl chlorid dissolved in 20 gr. carbon bisulfid and subjected to distillation; it is heated up to 120° C., to gain the remaining residue. The latter loses its specific petroleum odor.

(11.) 50 gr. refined petroleum are mixed with 2.5 gr. chromyl chlorid dissolved in 20 grains carbon bisulfid and filtrated. From this filtrate the carbon bisulfid is recovered by distillation, whereby it is heated up to 90° C. The residue shows a gray greenish color and represents the main part of the formed compounds.

The oil compounds of chromium thus generated possess great resistance against acids and alkalis and protect the iron against rust for a long time when used as paint or thinner respectively. They are distinguished from other means used for this purpose by the fact that they seemingly combine chemically with the iron, for, after they are brushed in and dried, which takes place in a short time, no "layer" is to be noticed on the iron, contrary to other protective means which stick mechanically to the iron. Iron treated with aforesaid oil compounds of chromium shows a beautiful black color, which can only be removed by filing, grind-

ing and the like. The iron thus prepared does not show an external layer after drying; it is unsusceptible to the detrimental influence of moisture, air and gas (oxygen, sulfurous acid, etc.) in general to the formation of rust. The oil chrome compounds which combine homogeneously with the iron, synchronize with its changes in dimensions; so that the former disadvantages of coats of paints, destruction of elasticity, cracking and blistering are done away with. Moreover salt solutions *e. g.* solutions of chlorid of sodium or chlorid of magnesium, (sea water) do not affect the iron.

Another advantage of these oil compounds of chromium consists in the fact that iron already covered with rust, after being impregnated, is protected against further rusting since the compound of chromium formed with or on the iron, eliminates the detrimental action of carbon dioxid, oxygen and moisture and converts partly the already formed rust.

When treating sub-marine buildings and the bottom of ships with these oil chrome compounds they prevent the settling of lower animal and vegetable organisms on account of the poisonous effect which extends uninterruptedly over the whole iron area, while the old means of this kind, which are only mechanically embedded in the varnish were removed, when the latter was destroyed, and left unprotected spaces. Tests have also shown that even metals can be dissolved in chromyl chlorid, as mercury, zinc, tin, though, of course, only in small quantities. The compounds thus generated impart a green black coloration to the oil or varnish treated with them. These preparations have the same advantages, as the previously named oil compounds of chromium, but according to circumstances are of a more poisonous character and are thus especially qualified for submarine buildings, bottom of ships, etc.

The described method may be used for the production of varnishes or siccatives. The described oil compounds of chromium may be used as vehicles. For many purposes it is a decided advantage to provide on top of the coat of the oil compounds of chromium another coat which contains as vehicles the oil compounds of chromium.

As mentioned above the following material may be subjected successfully to the described process: vegetable—as well as animal—and mineral oils, fats and different kinds of wax, resins and their distillation products, crude oil and its distillation product, mineral and fossil waxes, tar, fish-oil, mineral oil, lactescent products, bitumen (asphalt), crude turpentine oil, wood tar, anilin and similar hydrocarbons. Some of these materials, are simultaneously refined and deodorized.

I claim:—

1. In a process of producing a composition for impregnating or coating surfaces, more particularly for use as a rust preventive, the step of dissolving compounds of chromium having the same degree of oxidation as chromic acid in oils or fats.

2. In a process of producing a composition for impregnating or coating surfaces, more particularly for use as a rust preventive, the step of dissolving compounds of chromium having the same degree of oxidation as chromic acid in oils and fats, and preventing a violent reaction of said compounds on the oils or fats.

3. In a process of producing a composition for impregnating or coating surfaces, more particularly for use as a rust preventive, the step of dissolving chromyl chlorid in linseed oil under such conditions as to prevent a violent reaction.

4. In a process of producing a composition for impregnating or coating surfaces, more particularly for use as a rust preventive, the step of dissolving chromyl chlorid in oil and

adding a hydrocarbon to prevent a violent reaction.

5. In a process of producing a composition for impregnating or coating surfaces, more particularly for use as a rust preventive, the step of dissolving compounds of chromium in chlorinated oil.

6. In a process of producing a composition for impregnating or coating surfaces, more particularly for use as a rust preventive, the step of dissolving chromyl chlorid in chlorinated oil.

7. In a process of producing a composition for impregnating or coating surfaces, more particularly for use as a rust preventive, the step of dissolving chromyl chlorid in chlorinated oil and adding a hydrocarbon to prevent a violent reaction.

In testimony whereof I hereunto affix my signature in the presence of two witnesses.

DR. RUDOLF EBERHARD.

Witnesses:

A. V. W. COXE,
JOHANNA STERN.