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PROCESS FOR IMPARTING COLOR FINISH TO FERROUS METAL ARTICLES

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This application is a continuation in part of our previous application filed January 23, 1939, Serial No. 252,394, and application filed April 3, 1939, Serial No. 265,790. The invention relates to a soluble bath composition and method of using the same to impart a color finish to iron and steel articles by a process of oxidation.

It is applicable for use on ferrous metals generally, but is more particularly useful for steel and its alloys (except high chrome or stainless steel). On such steels for which it is applicable our process will impart a beautiful black finish which is somewhat rust protective in character. The finished surface also has a distinct lubricating character which adds to its wearing quality. This is of great value in the finished surface of working parts such as piston rings, cam shafts, gun mechanisms, etc.

The color finish obtained by the use of our product in the process hereinafter described is of the penetrating type and is applicable to steels whether in hardened or soft condition without build-up or thickening of the surface and may therefore be employed on finished tools and gauges without altering the dimensions thereof. For a satisfactory finish the degree of penetration into the surface may be in the order of .0003 or .0004 of an inch, and this surface will not peel, chip, or crack as is the case with the use of many prior art coating compositions.

According to the present invention our new product or bath comprises in aqueous solution a combination of a strong base and a readily oxidizing salt preferably from different members of the alkali metal group as for instance sodium hydroxide and potassium nitrates. Since in solution this composition would be indistinguishable if potassium hydroxide and sodium nitrate were chosen for the mixture, the selection of the original ingredients may be determined by consideration of market price. In the working of our process it is possible to use sodium as the metal constituent of both the hydroxide and nitrate compounds, or to use potassium in both said compounds, but compositions of this character are not as satisfactory as when different alkali metal radicals are used, one for the hydroxide compound, and the other for the nitrate compound.

The composition for the bath has the above named ingredients mixed in the proportion of one part of the nitrate to two parts of the hydroxide. For convenience in preparation of the bath and for marketing the products these ingredients may be fused together and molded into solidified cakes of the composition having a uniform distribution of said ingredients in the proportion stated.

In carrying out our process the composition thus obtained is dissolved in water and the solution is brought to its boiling point. The metal articles to be treated for oxidization and coloring are immersed in the bath while it is boiling, and the bath is kept boiling during said treatment. The boiling point temperature of the bath will of course depend on the concentration of composition in solution, viz. the proportion of water to composition in the bath. In other words the boiling point temperature will be increased above 212° F. (B. P. of pure water) in accordance with the amount of composition in solution. Keeping the bath boiling while in use for treating the metal articles serves a double purpose, first it insures an exact determination of temperature and concentration of the bath for the desired coloring effect on the articles and second, it keeps the bath in uniformly active oxidizing conditions as long as the bath exists. There will be no exhaustion of our bath as to its oxidizing activity irrespective of how many articles are treated therein or how long it is used.

In its more general aspect our process consists in the immersion of steel articles in a bath solution of the above composition while keeping the bath at its boiling point, the temperature of said bath and its corresponding concentration being sufficiently high to effect oxidation and coloring of said steel articles.

In its more particular aspects, our process consists in the treatment of said steel articles in successive stages, the first part of said treatment being carried out in a boiling bath at a relatively lower temperature than the temperature of said boiling bath for the last part of said treatment. While this progressive treatment may be carried out by immersion of the articles in one and the same vat wherein the boiling bath is allowed to gradually increase in concentration (by the boiling away of water) during the treatment, the commercial working of the process in this manner on a large scale would be slow and expensive because for each successive batch of articles to be treated, the bath would have to be reduced to its low starting temperature and subsequently raised to its high finishing temperature. We therefore propose as an important feature of our invention to carry out the process by distinct stages in separate bath vats whereby each bath can be kept at one temperature level and concentration. It will generally be found sufficient to use two such separate bath vats although more could be used in such progressive treatment if desired. The bath for the first stage treatment is maintained at the right boiling point and concentration for the preliminary oxidization and the articles after being immersed therein for the necessary period of time are immediately transferred into the second bath which is maintained at a higher boiling point and concentration for the finishing of said oxidization.

We will now describe in detail separate stages of our process as typical for treating the ordinary kinds of carbon steel articles to impart a black color finish thereto.

First stage

For the first stage of the process a solution is employed containing approximately 7¾ pounds of said composition to 1 gallon (approximately 8⅓ pounds) of water. A solution of this proportion and degree of concentration will have a boiling point very close to 285° F.

When first making up a bath it is desirable in order to avoid too violent a reaction and boiling over that only small quantities at a time of the above named composition be added to the water while it is being heated to the final boiling point. Inasmuch as during the time of reaching the right concentration of the bath, much of the original water will evaporate or boil away it is expedient to start preparing the bath with a surplus of water therein. For instance in our instructions to commercial users for initially preparing a bath, we advise that the operator add the composition little by little to the water in the proportion of 6½ pounds of composition per gallon of water, as the bath is being heated up to its final boiling point. When the bath is boiling at 285° F., or thereabouts, the operator will know that the right concentration is reached. At that boiling point temperature, viz. 285° F. the bath will actually contain in proportion 7¾ pounds of composition to each gallon of water or a concentration very close to said proportion.

When boiling at the temperature named the bath is ready for use and steel articles after being cleaned are immersed therein for a duration of about five to fifteen minutes for the ordinary work. However, in special kinds of work it may be necessary to continue the period of immersion for longer periods of anywhere up to sixty minutes, depending largely upon the physical characteristics of the articles being treated. The bath is kept constantly boiling at its predetermined boiling point temperature during use and by observing the temperature at which said boiling occurs, a control check is obtained upon the proportion of the composition in solution. Upon withdrawal from this bath the articles are immediately immersed in a second boiling bath of higher concentration but of the same composition in solution.

Second stage

In the second bath we employ approximately 9¼ pounds of said composition to 1 gallon of water, and this bath is likewise kept at its boiling point which at this concentration will be about 310° F. This second bath is prepared in the same manner as heretofore described for the first bath, viz. for each gallon of water initially in the bath 7½ pounds of composition is gradually added thereto until a final boiling point of 310° F. is obtained. When the boiling point temperature of 310° F. is reached, the proportion in the bath will be approximately 9¼ pounds of composition to each gallon of water.

The steel articles are immersed in this second bath generally for the same period of time as in the first bath although the duration of immersion in the second bath is subject to change for special kinds of work as described for the first bath. At the end of the second immersion the articles are removed from the bath, rinsed in water to remove solution, and put in a bath of protective oil for about five minutes. The work may then be removed and dried in sawdust or any convenient means.

After the first stage of treatment the articles will be partially oxidized and blackened but usually not to a satisfactory degree. After the second stage of treatment the steel articles will have received a beautiful black satin-like finish which is desirable for commercially satisfactory work.

In the foregoing example of our process we have mentioned particular boiling point temperatures and corresponding concentrations as being preferable for the average run of work, but it should be understood that said temperatures are not critical and are subject to variation depending on the kinds of steel being treated.

It is important, however, to keep the bath boiling during each stage of treatment and to maintain the concentration so that the boiling point temperature will be at the point wanted. It is also important to start treatment (preliminary oxidization) of the articles with the bath at a relatively lower temperature than for the finishing treatment (final oxidization). For obtaining uniform results on the same kinds of steel, day after day, and month after month, it will be convenient commercially to establish certain fixed boiling point temperatures for the bath at each successive stage and to maintain said established temperature levels by proper control of the concentration throughout each stage of treatment. Due to the fact that the bath of our composition when kept boiling does not exhaust or weaken in its oxidizing power during use, it is possible to obtain predictable and uniform results on the work by said control of the boiling point temperatures.

The most desirable boiling point temperature (and concentration) to be used in each stage and for every kind of steel or iron article cannot be named because of the almost unlimited variety in kinds, shapes and physical characteristics which pertain to such products. It will suffice to indicate the possible range of said temperature levels by pointing out a few examples. In treating very thin steel articles such as camera shutters, the first stage of treatment is best carried out in a bath of our composition at approximately a boiling point temperature of 230° F. and in a bath for the second stage of treatment at a boiling point of approximately 250° F. with corresponding concentrations. For high speed steels containing tungsten the first stage bath is preferably at 270° F. boiling point and the second stage bath at 290° F. boiling point. For steels having a hard rolled or hard drawn surface the second stage bath may be as high as 335° F. In this case as in all cases the temperature level of the bath for the first stage should be about 20° F. or more lower than that for the second stage bath. In general, the boiling point temperature for the first stage bath is established below the point which will oxidize the articles too severely as with a greenish or rust-colored scum and yet at a high enough point as will start the oxidization toward its black color. Other steels or steel articles than those mentioned may be developed which will require for best results different boiling point temperatures for the first stage bath and for the second stage bath than those we have named and we do not consider our invention as limited to any one particular boiling point temperature for either of said stage baths.

However, once the most suitable boiling point temperature is determined for a particular kind

of steel or article and for each stage of treatment of the same, it will be found desirable for uniform results to keep the boiling point temperature of the bath constant at the point fixed upon for each stage and throughout the period of immersion of work in that stage. In practice, easy and certain control of the above factors is obtained by watching the boiling point temperature. Any change of the boiling point temperature at once indicates a change in the concentration of the solution. If the boiling point temperature rises above the point desired more water is added,—if it falls, the excess water is allowed to boil away or more of the composition is added before using the bath. When the solution is boiling at the right boiling point temperature the operator will then know that there is the right proportion of composititon to water in the bath. Appropriate apparatus is available in the market for maintaining this control of boiling point temperature and concentration, automatically at any point desired. For instance, a water admission valve of the Barber-Colman type, may be used for intermittently feeding water into the bath tank under the control of a Foxboro type of temperature controller known as the "Rotax". The bath is heated by any one of the usual ways, sufficient to keep it boiling, and the above standard form of apparatus will work automatically to feed water into the bath as will be required for maintaining the boiling point temperature at the point established therefor.

The operation of the process may thus be carried out on a commercial scale for rapid and continuous production of work in the confidence that with uniformity of temperature, uniformity in concentration, and uniformity in oxidizing power of the bath; uniformity of a black color finish on the work will result.

We are aware of prior oxidizing salt baths which have been proposed for the same general purpose as herein described but said prior baths become exhausted after a brief period of use and require the addition of activating or regenerating agents to keep up their oxidizing power, irrespective of whether said prior baths are kept boiling. In our present bath no activating agent is required other than the effect of keeping the bath boiling when in use. In each stage of our process the bath solution as described does not deteriorate or exhaust in use and will give the same uniform oxidizing effect until the drag-out has removed the last drop of solution. For keeping the bath up in quantity to make up for drag-out losses, only the same original composition is added, and as above stated the percentage of water in the bath is continually regulated by the boiling point temperature required for each stage of the process.

We claim:

1. The process of treating the surface of ferrous metal articles to impart a black color thereto which consists in oxidizing said articles by immersion of the same in a salt bath, said bath comprising in aqueous solution, a composition of a nitrate and hydroxide, each of said compounds having a metallic constituent chosen from the alkali metal group, said compounds being in the approximate proportion of one part of said nitrate and two parts of said hydroxide, said treatment being conducted in successive stages, the bath for the preliminary oxidation of said articles having a concentration of composition in solution which boils at a temperature of about 20° F. to 25° F. lower than that of the bath for the final oxidation of said articles and controlling the operation of said bath for uniform action thereof, by keeping the bath boiling during each stage at substantially a constant temperature fixed for that respective stage.

2. The process of treating the surface of ferrous metal articles to impart a black color thereto which consists in oxidizing said articles by immersion of the same in a salt bath, said bath comprising in aqueous solution, a composition of a nitrate and hydroxide, one of said compounds having sodium as its metallic constituent and the other compound having potassium as its metallic constituent, said compounds being in the approximate proportion of one part of said nitrate and two parts of said hydroxide, said treatment being conducted in successive stages, the bath for the preliminary oxidation of said articles having a concentration of composition which boils at a temperature of about 20° F. to 25° F. lower than that of the bath for the final oxidization of said articles and controlling the operation of said bath for uniform action thereof, by keeping the bath boiling during each stage at substantially a constant temperature fixed for that respective stage.

3. The process of treating the surface of ferrous metal articles to impart a black color thereto which consists in oxidizing said articles by immersion of the same in a salt bath while the bath is boiling, said bath comprising in aqueous solution, a composition of a nitrate and hydroxide, each of said compounds having a metallic constituent chosen from the alkali metal group, said compounds being in the approximate proportion of one part of said nitrate and two parts of said hydroxide, said treatment being conducted in two successive stages, the first stage being an immersion of said article for a preliminary oxidation in such a bath having a concentration which boils at a temperature of about 285° F., the second stage being an immersion for the final oxidation in such a bath which boils at a temperature of about 310° F., and in each respective stage of said process keeping the bath boiling at a substantially constant temperature.

4. The process of treating the surface of ferrous metal articles to impart a black color thereto which consists in oxidizing said articles by immersion of the same in a salt bath while the bath is boiling, said bath comprising in aqueous solution, a composition of a nitrate and hydroxide, one of said compounds having sodium as its metallic constituent and the other compound having potassium as its metallic constituent, said compounds being in the approximate proportion of one part of said nitrate and two parts of said hydroxide, said treatment being conducted in two successive stages, the first stage being an immersion of said article for a preliminary oxidation in such a bath having a concentration which boils at a temperature of about 285° F., the second stage being an immersion for the final oxidation in such a bath which boils at a temperature of about 310° F., and in each respective stage of said process keeping the bath boiling at a substantially constant temperature.

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