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Improvement of color for iron oxide from waste pickling acid

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In this study, to improve the color of iron oxide from waste pickling acid at the cold rolling mill, quality control technologies to improve color were investigated. During operation of the spray roaster, the charge amount of waste acid per hour, temperature, and numbers of spray nozzles were investigated. At the admixing process, titanium oxide, silica, and goethite were tested. The color character of iron oxide can be improved by process control of the spray roaster and the admixing process at a pigment factory. Iron oxide from this study is appropriate for use as a colorant of a concrete product.

Keywords: iron oxide, colorant, waste acid, spray roaster

Introduction

During hot rolling, iron oxide scale is formed on the surface of steel sheet in ironwork due to a high-temperature oxidation temperature. Dense iron oxide scale acts as a defect on the steel sheet during cold rolling. Acid pickling is necessary to remove iron oxide scale from the surface of hot rolled steel sheet before cold rolling. Hydrochloric acid is the most commonly used pickling acid. During pickling, iron oxide scale is dissolved in the pickling acid mainly as $FeCl_2$ solution. After pickling, the waste pickling acid is regenerated as acid in the hydrochloric acid recovery facilities and iron oxide is recovered by using a spray roaster (1). Regenerated acid is recycled as pickling acid. Iron oxide, which originates as a by-product of the pickling process, is used as raw material for soft and hard ferrite, and a component of iron oxide is also used as red and brown raw material in the pigment industry to color brick and tiles (2,3). There are several manufacturing processes of iron oxide for pigment. The hydro process is well known as a synthetic procedure to utilize iron oxide for pigment. Iron oxide from the hydro process is high quality pigment but the manufacturing cost is expensive compared with the spray roaster process. Iron oxide from the spray roaster procedure is cost effective but improvements were needed in the pigment's properties (4). During the past several years, there has been a demand in Korea for improvements in the color of iron oxide derived from a spray roaster. This study investigated the spray roaster process and admixing process to improve the color properties of iron oxide from waste pickling acid at cold rolling mills.

Spray roaster

For the recycling of waste pickling acid from steel making, there are several commercial processes, such as a spray roaster process, fluidized bed process, and hydro process. The most commonly used one is a spray roaster process. The spray roaster process is a well-established process in steel manufacturing. A schematic figure of a spray roaster is shown in Fig. 1.

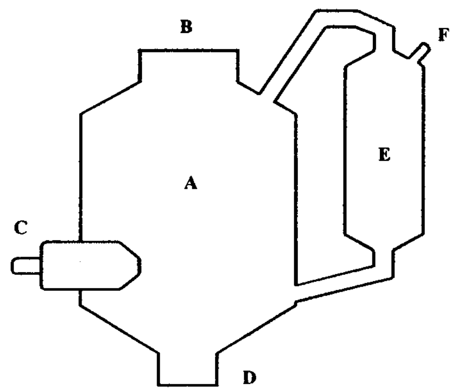


Fig.1 Schematic drawing of spray roaster
A: Spray roaster B: Spray nozzle
C: Burner D: Iron oxide extruder
E: Cyclone F: Cl_2 gas outlet

In the typical spray roaster process, waste pickling acid is released from spray nozzles at the top of the roaster. The type and number of spray nozzles operating are different in each company. When waste pickling acid is sprayed into the roaster, it forms small droplets, and moves downward. Otherwise, burners installed on the sidewall blow hot air upward in the roaster. Droplets of pickling acid meet the hot air in the central section of the roaster. The hot air reacts with the liquid waste acid and forms a solid iron oxide layer on the surface of the droplet. Waste pickling acid reacts according to the following equation: (1)

$$2\ FeCl_2 + 1/2\ O_2 + 2H_2O = Fe_2O_3 + 4HCl$$

During the reaction, the vapor pressure of the liquid in the inner part of the droplet is increased rapidly. Finally, the droplet is broken into small particles of iron oxide. If the oxidation reaction was insufficient, $FeCl_2$, FeO, Fe_2O_3, and a mixture of FeO-Cl_2 are formed. For $FeCl_2$ to be decomposed sufficiently, it is necessary to increase the temperature, air ratio and number of nozzles, and to decrease the amount of spray. During the reaction, relatively heavy weight iron oxides drop to the bottom of the roaster and are extracted. Relatively lightweight particles of iron oxides and Cl_2 gas overflow to a cyclone. In a cyclone, iron oxide particles move downward and are returned to the spray roaster. During the cycling reaction, lightweight particles become heavy, and drop to the bottom of the roaster. In the process, Cl_2 gas moves to the HCl Recovery Acid Facility and is recycled as pickling acid. The spray roaster temperature is critical because as the operation temperature increases; sintering of iron oxide increases and shortens the lifespan of the refractory. As operation temperatures increase, iron oxide particles increase in size because of the sintering reaction and the color becomes darker (3,4). In the field, the spray roaster's operation condition depends on the amount of waste acid generated from a pickling line and the capacity of the spray roaster. When the amount of waste acid increases, the operating temperature of the spray roaster is increased to expand the unit's capacity.

Experiment

Spray roaster

Operation parameters of a spray roaster used in the waste pickling recovery process were tested at the cold rolling mill in P steel company. To analyze the relationship between operation condition of the spray roaster and the color of iron oxide produced, the operation temperature, spray amount of waste pickling acid (l/hr), number of spray nozzles for waste pickling acid, and air ratio (flow rate of additional air + the standard air/ flow rate of the standard air) of the spray roaster's atmosphere were examined

Admixing of colorants

For the improvement of iron oxide color, colorants such as titanium oxide, silica, and goethite were used. Colorant was gradually added to the iron oxide up to 20 wt%. Each sample was mixed in a ball mill for 20 min., and then its color index was determined by a color meter.

Results and Discussion

Spray roaster

The operation results of the spray roaster are shown in Table 1. In the spray roaster experiment, operation temperature was controlled from 550 °C to 600 °C. Generally, the iron oxide color is lighter when the spray roaster is operated at a lower temperature. However, in this spray roaster, 550° C is the lowest possible operating temperature because the decomposition rate of Fe and Cl in $FeCl_2$ is inadequate at lower temperatures. The Cl content in iron oxide is too high to use as a colorant.

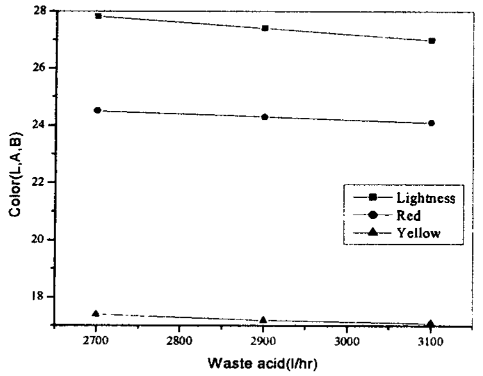
Table 1 Color of iron oxide from the operation of a spray roaster.

Operation Condition	Temp	Flow rate (l/hr)	No. of nozzle	Air ratio	Lightness	Red	Yellow
1	580	2700	14	1.35	27.82	24.63	17.40
2	580	2900	14	1.35	27.43	24.36	17.19
3	580	3100	14	1.35	26.98	24.01	17.08
4	550	2900	14	1.35	25.11	23.15	15.79
5	560	2900	14	1.35	25.76	23.13	16.24
6	600	2900	14	1.35	27.26	24.37	17.20
7	580	3100	14	1.4	27.42	23.95	16.52
8	580	3100	21	1.35	27.59	23.83	16.57
9	580	4050	21	1.35	26.17	21.89	13.83
10	580	4650	21	1.35	24.92	21.19	13.31
11	550	3100	21	1.35	30.68	24.83	18.14
12	560	3100	21	1.35	28.92	23.27	17.16
13	600	3100	21	1.35	27.05	22.92	15.40
14	580	3100	21	1.4	28.85	23.38	[illegible]

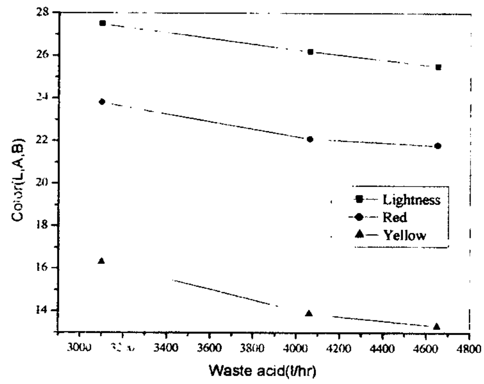
When the flow rate is fixed and the spray nozzles are increased from 14 ea. to 21 ea., the amount of acid spray is decreased from 221 l/hr to 148 l/hr per nozzle. With 21 nozzles in operation, the amount of acid spray from each nozzle is decreased, but the total surface of each droplet is increased compared to operations using 14 nozzles. By increasing the total surface area, the roasting reaction rate is increased. Generally, lightness of iron oxide depends on the roasting reaction rate. When the flow rate was increased, the lightness of iron oxide increased while red and yellow decreased.

Changes of the air ratio at the spray roaster revealed that as the air ratio increased, the lightness of iron oxide increased while red and yellow decreased slightly. These results are explained by the roasting reaction rate. During the oxidation reaction, decomposed Fe became Fe_3O_4, in the intermediate phase and finally Fe_2O_3. The color of Fe_3O_4 is black while the color of Fe_2O_3 is red. When atmospheric oxygen increases, decomposed Fe oxidizes sufficiently and becomes Fe_2O_3. The experiment demonstrated that with 21 nozzles, as the oxygen ratio increased from 1.35 to 1.4, the lightness of iron oxide increased rapidly from 24.92 to 28.85. At the operation condition No. 10 in Table 1, $FeCl_2$ is decomposed insufficiently due to the low operation temperature and air ratio. Therefore, $FeCl_2$ and Fe_3O_4, in the intermediate phase failed to convert to Fe_2O_3. The resultant iron oxide has a dull color and high chlorine content.

The effect of spray amount in a spray roaster on the color of iron oxide is shown in Fig.2. When the spray amount increases, the color of iron oxide decreases. Increases in the spray amount cause $FeCl_2$ to decompose insufficiently. The intermediate phase in iron oxide appears to negatively affect the color of iron oxide.



(A)



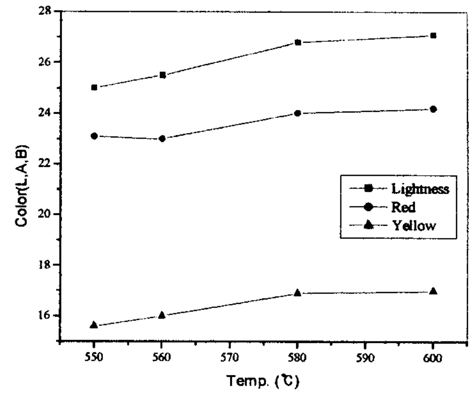
(B)

Fig.2 Effect of charge amount of waste acid on color of iron oxide in spray roaster process

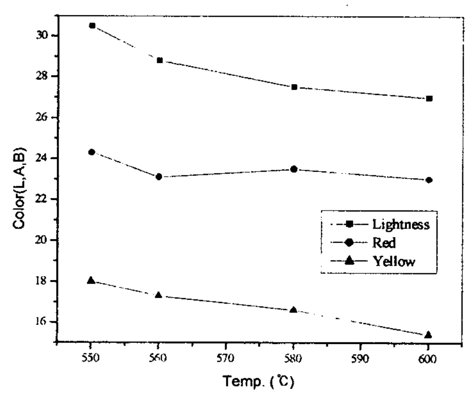
(A) No. of 14 nozzles, Temp. 580℃

(B) No. of21 nozzles, Temp. 580℃

Fig. 3 shows the affect of operation temperature on the color of iron oxide. With 14 nozzles, the color of iron oxide was improving as the temperature increased. The operation temperature, 540 °C was not high enough to decompose $FeCl_2$, so increasing the temperature, improved the color of iron oxide. On the contrary, with 21 nozzles, the reverse was found. These results can be explained by the spray amount per nozzle. With 14 nozzles, the waste acid spray amount is 207 l/hr, but with 21 nozzles, it is 148 l/hr. With 21 nozzles, the spray amount per nozzle is relatively small, and the operation temperature of 550° C is enough to completely decompose $FeCl_2$. Therefore, when temperature is increased, sintering of particles occurs. The resultant increase in particle size decreases the color of iron oxide.



(A)



(B)

Fig.3 Effect of operation temperature on color of iron oxide in spray roaster process

(A) No. of 14 nozzles, flow rate 2900 l/hr

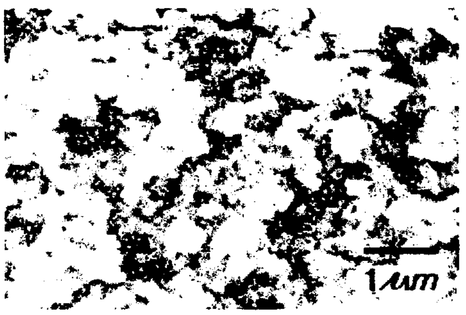
(B) No. of21 nozzles, flow rate 3100 l/hr

Admixing of colorants

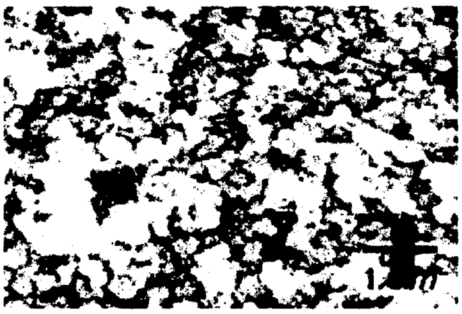
Table 2 lists the color index of colorant for admixing. Compared to iron oxide, titanium oxide and silica show a relatively high value of lightness. Goethite has a medium value of lightness and yellow. Concerning lightness, colorants are relatively superior to iron oxide. However, concerning red, colorants are inferior to iron oxide.

Table 2 Color index of iron oxide and colorant

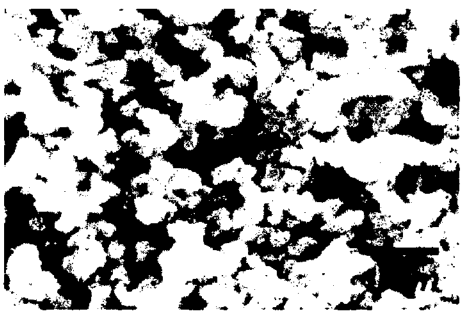
Materials	Lightness	Red	Yellow
Iron oxide	29.19	27.37	21.06
Titanium oxide	94.17	0.03	4.82
Silica	92.50	-0.02	2.32
Goethite	56.30	16.62	54.79



(A)



(B)



(C)

(D)

Fig. 4 Photograph of iron oxide and colorant used in admixing test

A: Iron Oxide B: Titanium Oxide
C: Silica D: Goethite

Concerning red, minus value means green color in the CIE Lab color system. (5) The shape of iron oxide and colorants are shown in Fig. 4. Iron oxide appeared to have a spherical shape and the average grain size was 5㎛. The grain shapes of titanium oxide and silica were spherical and the average grain size was 0.2㎛. In addition, the grain shape of goethite was acicular with an aspect ratio 10 and the average grain size was 1㎛.

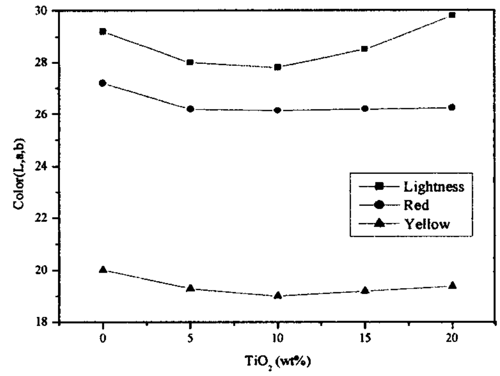


Fig.5 Effect of titanium oxide colorant on color of iron oxide

The results of admixing titanium oxide colorant to iron oxide are shown in Fig. 5. Theoretically, when white material is added to iron oxide, it is expected that lightness will be increased in the modified iron oxide. However, from the results of this study, lightness of modified iron oxide from 5 wt.% to 15 wt.% are lower than the original iron oxide. Only with 20% modified iron oxide is the lightness slightly higher than the original iron oxide. From the experimental results, it can be suggested that during the admixing process, titanium oxide grains are too small to achieve homogeneous admixing with the iron oxide grains, and this heterogeneous admixing affect slightly reduces the lightness of the modified iron oxide. Concerning red, the minus value of red color of titanium oxide affected the modified iron oxide. As the amount of titanium oxide was increased, the red of the modified iron oxide decreased slightly. Concerning yellow, as the added amount increased from 15 wt.% of titanium, the yellow of the modified iron oxide increased slightly.

The color of the iron oxide modified by silica is shown in Fig. 6. As the amount of silica increased, the lightness of the modified iron oxide increased. Compared to titanium oxide, silica admixed more homogeneously with iron oxide. However, from the gap of grain size between silica and iron oxide, the lightness of the modified iron oxide increased steeply from 15 wt% of silica added.

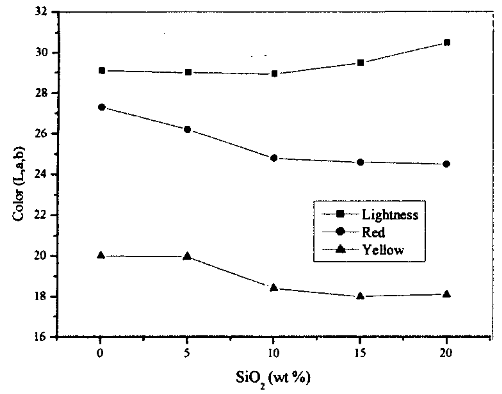


Fig.6 Effect of silica colorant on color of iron oxide

Results obtained from admixing goethite colorant in iron oxide are shown in Fig. 7. When goethite was mixed with iron oxide, lightness was increased steeply, but red was decreased slightly. The Color of iron oxide was changed to bright orange. Compared to titanium oxide and silica, goethite is the most effective colorant to improving of lightness of iron oxide.

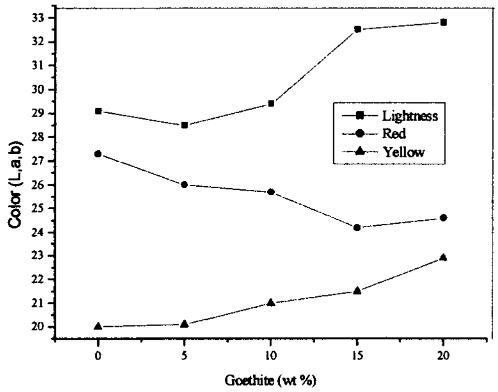


Fig.7 Effect of goethite colorant on color of iron oxide

Conclusion

To improve the color of iron oxide from a spray roaster process, the operation condition of the spray roaster and the admixing process were examined. The results of this study are summarized as follows:

1. The color of iron oxide can be improved by control of the spray roaster and admixing processes.

2. From the operation test of a spray roaster, the optimum operation conditions for iron oxide pigment are: temperature 550℃, flow rate 3100 l/hr, number of nozzles 21, air ratio 1.35.

3. Compared to titanium oxide and silica, goethite is the most effective colorant for improving the lightness of iron oxide in this admixing experiment.

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