Preparation Technology of Water Based Detergent for Q235 Carbon Steel

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Abstract. Q235 carbon steel is smelted by a converter or open-hearth furnace. However, it is always speckled with oil in the manufacturing process influencing its use performance. In the paper, a water-based detergent, a variety of surfactants and additives, was used to remove the oil. First, the three remarkable surfactants were selected through single-factor experiment. Then, surfactants composition was obtained by simplex formula design. Finally, the optimum formula of metal cleaner was obtained by the uniform experimental design: FMEE 1%, MOA5 2.4%, 6501 2.6%, foam inhibitor 3%, antitrust agent 2.4%+AES 2%+ carboxylic acid inhibitor 1.7%+copper corrosion inhibitor 2.1%+ detergent auxiliary 1.9%+water 80.9%. The cleaning efficiency can reach more than 98%.

Key words: Simplex formula design; Water-based detergent; Uniform experiment; Cleaning efficiency.

1. Introduction
Due to the state's urban construction plan in recent years, the demand for Q mild carbon steel (Q235) has increased greatly. The production process of Q235 section steel includes anti-corrosion coating, surface cleaning, electroplating, and others. The cleaning efficiency of surface oil stains in the cleaning process directly affects the electroplating effect and the quality of the steel, So it has become an extremely important and hot topic that the surface cleaning of the oil for Q235. In recent years, many kinds of metal cleaner have been developed by our country. But because of its cleaning rate, defoaming, rust resistance, stability, and other technical performance indicators can not meet the needs of industrial production, meanwhile, the costs of production are also expensive high[1]. Most of the commercial cleaning agents have higher requirements on the use conditions and have greater harm to the human body and the environment[2]. Therefore, three kinds of surfactants that have the greatest influence on the cleaning efficiency were selected through single-factor experimental design. The proportions of various surfactants were determined by simple formula design, and the optimal proportions were optimized by uniform experiment. It has been proved by experiments that this water-based cleaning
agent formula is an optimal choice with high cleaning efficiency of 98.6% and low cost at room temperature.

2. Surface Oil Composition Analysis of Q235

In order to protect the performance of Q235, people will be oil treatment in the production and processing process, but before welding, oil, rust, water will be cleaned, so as to avoid producing hydrogen gas that is harmful to welding. Oil pollution in industry can be divided into two main types, saponification oil and non-saponification oil. Saponification oil is mostly a variety of fatty acid glycerides, mainly animal and plant oil, they can saponification reaction with alkali to produce soap and glycerin; Non-saponification oil is generally a variety of hydrocarbons, mainly mineral oil. They can't saponify with bases to form water-soluble substances.[3]

3. Materials & Methods

3.1. Preparation of typical industrial oil stains

This paper uses GB/T 35759-2017 to prepare industrial oil pollution. The manually prepared oil composition is as follows (in terms of quality): Barium sulfonate 8%, lanolin magnesium soap 3.5%, lanolin 2%, industrial vaseline 30%, no. 20 machine oil 34.5%, no. 30 machine oil 12%, calcium base grease 2%, alumina 8%. Heat the mixture of industrial vaseline, no. 20 machine oil and no. 30 machine oil according to a certain formula; Melt and stir evenly, add lanolin magnesium soap(NA), barium petroleum sulfonate, calcium base fat, stir and dissolve. After all dissolved, stop heating, add alumina powder, stir evenly and cool to room temperature, store in a drying oven for later use.

3.2. Preparation of cleaning agent

Appropriate FMEE, moa-5, 6501, foam inhibitor, rust inhibitor, AES, carboxylic acid corrosion inhibitor, copper corrosion inhibitor, detergent auxiliary, etc were weighed with electronic balance, and add a proper quantity of water. 50ml beaker was placed in turn into a magnetic stirrer and stir it; set aside.

Drug information used in this project experiment are shown in Table 1

| Name                  | Content       | Manufacturers                                | Purity          |
|----------------------|---------------|----------------------------------------------|-----------------|
| Amide (6501)         | 95%           | Wuhan mengqi technology co. LTD              | analytic reagent|
| polyethylene glycol, | 5%            | Hai ‘a petrochemical plant, jiangsu province | analytic reagent|
| PEG                  |               |                                              |                 |
| Coconut oil fatty     | 99.5%         | Hai ‘a petrochemical plant, jiangsu province | analytic reagent|
| OP-10                | 36%-38%       | Tianjin zhiyuan reagent co. LTD              | analytic reagent|
| PAODI-GPE            | 99.9%         | Hai ‘a petrochemical plant, jiangsu province | analytic reagent|
| FMEE                 | 36.0～38.0%   | Guangzhou source chemical industry          | analytic reagent|
| MOA-5                | ≥30.0%        | Hai ‘a petrochemical plant, jiangsu province | analytic reagent|
| AES                  | 95.0～98.0%   | Guangzhou lam xin chemical co., LTD         | analytic reagent|
| Carboxylic acid      | 97.0～100.5%  | Sinopharma chemical reagent co. LTD         | analytic reagent|
| corrosion inhibitor  |               |                                              |                 |
| Corrosion inhibitor  |               |                                              |                 |
| for copper           | ≥99.8%        |                                              |                 |
| PAA                  | 25.0～28.0%   |                                              |                 |
3.3. Experimental Scheme

3.3.1. Test Flow and Test Method of Cleaning Efficiency. Cut Q235 section steel into 2cm*3cm steel sheet and measure its weight as \( m_0 \). Covered it with industrial oil, then it was put into a vacuum drying oven at 80°C, dried for 30min, and measured its mass as \( m_1 \) after it was taken out. After oiling, the steel sheet was put into the solution of the prepared cleaning agent, cleaned with ultrasonic cleaning instrument, and then washed with water after taking it out at 25°C for 15min. After taking it out, rinsed it with water, dry it and weigh its mass \( m_2 \) to calculate the cleaning efficiency \( X \).

\[
X = \frac{m_1 - m_2}{m_0 - m_2} \times 100\%
\]

(1)

\( X \)- cleaning efficiency, %

\( m_0 \)- The quality of iron sheet before oiling, g

\( m_1 \)- The quality of the iron plate after oiling, g

\( m_2 \)- Quality of iron sheet after cleaning, g

The experimental equipment and models used in this project are shown in TABLE 2

| Name                        | Model     | Manufacturers                                      |
|-----------------------------|-----------|---------------------------------------------------|
| Glass apparatus             | Various   | Sichuan shuniu glass (group) co. LTD              |
| Vacuum drying oven          | DZF-6032  | Shanghai yiheng scientific instrument co., LTD    |
| Collector type constant     | DF-101S   | China laboratory equipment sales center           |
| temperature magnetic agitator|           | Mai yi scientific instrument co. LTD              |
| Precision Electronic Balance| BSA124S   | Kunshan sumei ultrasonic cleaner                  |
| Ultrasonic cleaner          | KQ-250E   |                                                   |

3.4. Experimental Design for Determining the Optimal Compounding Ratio of Surfactants

① One-factor experimental design

The cleaning efficiency of surfactant solutions with concentrations of 2.0%, 2.5%, 3%, 3.5% and 4% were tested.

② Simplex formula design

![Figure 1. Design principle of single grid formula](image)

Simplex formula design: according to the performance of the product required conditions and process requirements, through a number of tests, optimization, reasonable selection of required raw materials,
determine the proportion of raw materials. It is a special mixed material test design application, through the qualitative and quantitative analysis of each test component, after the test index, then the mixed material regression design.

The surfactant was compounded by the experimental design of single lattice formula and four levels were set.

Table 3. Formula design of a single grid

| Test number | Z1 | Z2 | Z3 |
|-------------|----|----|----|
| 1           | 1  | 0  | 0  |
| 2           | 0  | 1  | 0  |
| 3           | 0  | 0  | 1  |
| 4           | 2/3| 1/3| 0  |
| 5           | 1/3| 2/3| 0  |
| 6           | 2/3| 0  | 1/3|
| 7           | 1/3| 0  | 2/3|
| 8           | 0  | 2/3| 1/3|
| 9           | 0  | 1/3| 2/3|

3.5. Uniform Experiment To Determine The Experimental Design of Cleaning Agent Formula

Through the uniform experiment, the optimum ratio of various water-based active cleaning agents and various dispersant was designed.

Table 4. The composition list of uniform experiment

| No. | A  | B  | C  | D  | E  | F  | G  | Y            |
|-----|----|----|----|----|----|----|----|--------------|
|     | level factoria | Surfactant mass fraction % | Washing aid mass fraction % | Foam inhibitor mass fraction % | Antirust agent mass fraction % | Carboxylic acid inhibitor mass fraction % | Copper corrosion inhibitor mass fraction % | PAA concentration mass fraction % | Washing efficiency and mass fraction % |
| 1   | 1  | 2  | 3  | 4  | 5  | 7  | 10 |              |
| 2   | 2  | 4  | 6  | 8  | 10 | 3  | 9  |              |
| 3   | 3  | 6  | 9  | 1  | 4  | 10 | 8  |              |
| 4   | 4  | 8  | 1  | 5  | 9  | 6  | 7  |              |
| 5   | 5  | 10 | 4  | 9  | 3  | 2  | 6  |              |
| 6   | 6  | 1  | 7  | 2  | 8  | 9  | 5  |              |
| 7   | 7  | 3  | 10 | 6  | 2  | 5  | 4  |              |
| 8   | 8  | 5  | 2  | 10 | 7  | 1  | 3  |              |
| 9   | 9  | 7  | 5  | 3  | 1  | 8  | 2  |              |
| 10  | 10 | 9  | 8  | 7  | 6  | 4  | 1  |              |

Table 5. Uniform experimental design table

| No. | A  | B  | C  | D  | E  | F  | G  |
|-----|----|----|----|----|----|----|----|
| 1   | 1  | 2  | 3  | 4  | 5  | 7  | 10 |
| 2   | 2  | 4  | 6  | 8  | 10 | 3  | 9  |
| 3   | 3  | 6  | 9  | 1  | 4  | 10 | 8  |
| 4   | 4  | 8  | 1  | 5  | 9  | 6  | 7  |
| 5   | 5  | 10 | 4  | 9  | 3  | 2  | 6  |
| 6   | 6  | 1  | 7  | 2  | 8  | 9  | 5  |
| 7   | 7  | 3  | 10 | 6  | 2  | 5  | 4  |
| 8   | 8  | 5  | 2  | 10 | 7  | 1  | 3  |
| 9   | 9  | 7  | 5  | 3  | 1  | 8  | 2  |
| 10  | 10 | 9  | 8  | 7  | 6  | 4  | 1  |
4. Results and Discussion

4.1. Determine The Optimal Compounding Ratio of Surfactants

4.1.1. Single factor analysis of variance. A single factor experiment was conducted to study the effect of 6501 on cleaning efficiency, as shown in the FIG2

![Figure 2](image)

**Figure 2.** Effect of 6501 concentration on cleaning efficiency

It can be seen from figure 2 that the cleaning efficiency reaches the highest when its proportion is 2.5%. With the increase of concentration, the diffusion rate of surfactant molecules from the body to surface increases, when the concentration of surfactant is higher than the CMC of surfactant[4]. The value of the expansion modulus of the mixed system is close to that of a single surfactant solution, indicating that the large molecules are replaced gradually by surfactant molecules on the interface, which results in the decrease of their effective cleaning concentration [5]. That is, the cleaning efficiency of 6501 began to decrease after the concentration reached 2.5%.

Single-factor experiment was conducted to study the influence of the proportion of op-10 concentration in the cleaning agent on the cleaning efficiency, as shown in figure 3.

![Figure 3](image)

**Figure 3.** Effect of op-10 concentration on cleaning efficiency

With the increase of op-10 concentration, the cleaning effect changed little. This is due to the op-10's ability to reduce liquid surface tension and inhibit crude oil back fouling. However, with the increase of concentration, due to the good hydrophilicity of op-10, the formation of a multi-molecular membrane in the solution resulted in relatively large solution viscosity, making the cleaning efficiency basically unchanged.
The single-factor experiment was conducted to study the influence of the proportion of FMEE concentration in detergent on washing efficiency. The results are shown in figure 4.

![Figure 4. Effect of FMEE concentration on cleaning efficiency](image)

In the beginning, with the increase in the concentration of FMEE, the cleaning effect gradually decreased. At the concentration of 2.5%, the cleaning efficiency was the lowest. After this, cleaning efficiency has a significant recovery. It can be inferred that with the increase of FMEE concentration, the dispersion of surfactant becomes smaller due to the influence of calcium and magnesium ions in water, thus reducing the cleaning efficiency.

Single-factor experiment was conducted to study the influence of the proportion of MOA-5 concentration in detergent on washing efficiency. The results are shown in figure 5. With the addition of surfactant, the interface of dispersed phase particles will form an interface membrane that can effectively reduce the interfacial tension. Due to the existence of the interface membrane, the surface structure of dispersed phase particles changes, which affects the motion of dispersed phase particles. Therefore, the cleaning efficiency decreases slightly when the volume proportion of moa-5 is 2.5%. As the volume of moa-5 increases, the surfactant molecules form an interfacial membrane in a neat, tightly packed state. This makes the viscosity of the dispersion system reach the maximum, while the dispersion system exists in a relatively stable state[6]. This is why cleaning efficiency is highest when moa-5 is 2%. As the volume of moa-5 increases, the cleaning efficiency decreases. This is because, with the increase of the volume of moa-5, the stability of the dispersed system gradually increases, which leads to the weakening of the cleaning effect.

![Figure 5. Effect of MOA-5 concentration on cleaning efficiency](image)
The single-factor experiment was conducted to study the influence of the proportion of polyethylene glycol concentration in detergent on washing efficiency. The results are shown in figure 6.

![Figure 6. Effect of polyethylene glycol concentration on cleaning efficiency](image)

As can be seen from figure 6, adding the right amount to polyethylene glycol can promote the reaction because water can reduce the viscosity of PEG 1000-DIL [7], and it would improve the rate of mass transfer. However, if the water content is too high, the ionic liquid concentration will be diluted, which will reduce the yield. When the content of polyethylene glycol is around 2.5%, the cleaning effect is the best. When the concentration is too low, it is not conducive to cleaning and the corrosion of the cleaning agent cannot be inhibited. With the increase of PEG concentration, the cleaning effect of water-based cleaning agent solution is gradually enhanced, which can also prevent the corrosion of steel. The reason is that the hydrogen bond was broken, causing the ionic liquid to behave as a lipophilic liquid. When the concentration of the active agent is too high, the ionic liquid is relatively viscous. The products are difficult to separate and the solution becomes less homogeneous, preventing the reactants from coming into full contact with it and eventually leading to corrosion of the aluminum sheet.

Through the above six single factor experiments, we can get the following conclusions: The concentration of 6501, FMEE and moa-5 has a great influence on the cleaning efficiency. Therefore, we selected 6501, FMEE and moa-5 as the main components of the complex surfactant.

4.1.2. Simplex Lattice Experimental Analysis. The experimental results of simplex formula design are shown in table 6

| No. | A(The proportion of 6501) | B(The proportion of FMEE) | C(The proportion of MOA-5) | Y( Cleaning efficiency %) |
|-----|--------------------------|---------------------------|---------------------------|--------------------------|
| 1   | 1                        | 0                         | 0                         | 0.9217                   |
| 2   | 0                        | 1                         | 0                         | 0.8756                   |
| 3   | 0                        | 0                         | 1                         | 0.9008                   |
| 4   | 2/3                      | 1/3                       | 0                         | 0.6681                   |
| 5   | 1/3                      | 2/3                       | 0                         | 0.9209                   |
| 6   | 2/3                      | 0                         | 1/3                       | 0.7582                   |
| 7   | 1/3                      | 0                         | 2/3                       | 0.7981                   |
| 8   | 0                        | 2/3                       | 1/3                       | 0.9999                   |
| 9   | 0                        | 1/3                       | 2/3                       | 0.9999                   |
After the regression analysis, the experimental results are obtained, and the regression equation is as follows:

\[ Y = 0.0389A + 0.0922B + 0.0868C + 0.6536 \]  

(2)

According to the results of the experiment, FMEE concentration was the most influential factor, followed by moa-5 concentration and 6501 concentration. By solving the regression equation derived from the test results, it can be concluded that the optimal concentration ratio of FEMM, MOA-5 and 6501 is 1:2.4:2.26. After that, we verified through experiments that the washing efficiency under this ratio was 95.3%.

4.2. Determination of Cleaning Agent Formula by Uniform Experiment

We designed 7 factors (surfactant, detergent assistant, foam inhibitor, rust inhibitor, carboxylic acid corrosion inhibitor, copper corrosion inhibitor, and PAA concentration), 10 levels of uniform test, as shown in Table 7.

After the experimental results are processed and analyzed by DPS, the direct and indirect path coefficients are obtained. The effect factors of each experimental factor on the experimental results and a series of determinants can be calculated by the formula. The results are shown in Table 8. The decision coefficients are then ranked from large to small so that we can find out the main factors influencing the outcome variable and the degree of interaction.

| No. | A | B | C | D | E | F | G | Y  |
|-----|---|---|---|---|---|---|---|----|
| level factoria | Surfactant mass fraction | Washing aid mass fraction | Foam inhibitor mass fraction | Antirust agent mass fraction | Carboxylic acid inhibitor mass fraction | Copper corrosion inhibitor mass fraction | PAA concentration mass fraction | Washing efficiency and mass fraction |
| 1   | 4 | 4.5 | 5 | 5.5 | 6 | 7 | 8.5 | 92.16 |
| 2   | 4.5 | 5.5 | 6.5 | 7.5 | 8.5 | 5 | 8 | 95.26 |
| 3   | 5 | 6.5 | 4 | 5.5 | 8.5 | 7.5 | 8.5 | 99.99 |
| 4   | 5.5 | 5.5 | 6 | 7.5 | 8 | 5 | 6.5 | 76.87 |
| 5   | 6 | 8.5 | 4.5 | 6.5 | 4.5 | 7.5 | 8 | 93.58 |
| 6   | 6.5 | 4 | 4 | 7.5 | 4.5 | 6.5 | 5.5 | 98.68 |
| 7   | 7 | 6 | 6.5 | 7.5 | 6 | 5 | 4 | 99.99 |
| 8   | 7.5 | 5 | 6 | 4 | 7.5 | 6.5 | 4 | 97.54 |
| 9   | 8 | 5 | 6.5 | 7 | 4 | 7.5 | 4 | 94.48 |
| 10  | 8.5 | 8 | 7.5 | 7 | 5.5 | 4 | 94.48 |

According to the data results, the influence degree of the independent variables X1, X2 and X3 on the outcome variable Y is ranked as X1 > X3 > X2.
The indirect path coefficient of the influence of the independent variable $X_1$ on the outcome variable through the independent variable $X_2$ is -0.0647.

The indirect path coefficient of the influence of the independent variable $X_1$ on the outcome variable through the independent variable $X_3$ is 0.0208.

The indirect path coefficient of the influence of the independent variable $X_2$ on the outcome variable through the independent variable $X_1$ is 0.0969.

The indirect path coefficient of the influence of the independent variable $X_2$ on the outcome variable through the independent variable $X_3$ is -0.0208.

The indirect path coefficient of the influence of the independent variable $X_3$ influencing the outcome variable through the independent variable $X_1$ is 0.0581.

The indirect path coefficient of the influence of the independent variable $X_3$ on the outcome variable through the independent variable $X_2$ is 0.0388.

A series of decision coefficients can be calculated by formula[8]. Then rank the decision coefficients from large to small to find out the main factors that affect the outcome variables and the degree of interaction. After the experimental results are processed by DPS, the direct and indirect path coefficients can be obtained[9]. After calculation, the effect factors of each experimental factor on the experimental results and the regression equation can be obtained, $0.0066X_1-0.0044X_2+0.0024X_3+0.9296=Y$. According to the regression equation, the best formula of stainless steel metal cleaner is FMEE 1%+MOA-5 2.4%+6501 2.6%+ Foam inhibitor 3%+ rust inhibitor 2.4%+ AES 2%+ carboxylic acid corrosion inhibitor 1.7%+ copper corrosion inhibitor 2.1%+ washing assistant 1.9%, and water 80.9%. The washing efficiency was 98.6%.

5. Conclusion

6501, FMEE and MOA-5 were selected as the active ingredients of mixed surfactants through single-factor experiments. Then, through simplex formula design, we obtained the factors that had the greatest influence on the cleaning efficiency, in which the concentration of FMEE was the biggest influence, followed by the concentration of MOA-5 and the concentration of 6501. The optimal concentration ratio of FMEE, MOA-5 and 6501 is 1:2.4:2.26. Under this ratio, we verified through experiments that its washing efficiency was 95.3%. Finally, the uniform experimental design was used to optimize the metal cleaner formula. A new metal cleaner with excellent performance and low cost were obtained. Its best formula is FMEE 1%+MOA-5 2.4%+6501 2.6%+ Foam inhibitor 3%+ rust inhibitor 2.4%+ AES 2%+ carboxylic acid corrosion inhibitor 1.7%+ copper corrosion inhibitor 2.1%+ washing assistant 1.9%, water 80.9%. Through three parallel experiments, we verified that the washing efficiency of this cleaning agent was 98.6%.

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