Journal of the University of Chemical Technology and Metallurgy, 43, 3, 2008, 315-318

PROTECTIVE COATINGS FOR METAL SURFACES FROM ETHYL ESTERS OF FATTY ACIDS AND WASTE PRODUCTS OF THE OIL INDUSTRY

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Received 04 February 2008
Accepted 12 August 2008

ABSTRACT

Three types of protective coatings based on ethyl ester of stearic acid, ethyl ester of oleic acid and ethyl ester of tall oil fatty acids and by-products of the petroleum refining industry were studied. The physical-chemical properties of the coatings were investigated. The best-protected holding is that on the base of ethyl ester of tall oil fatty acids.

Keywords: protective coatings, ethyl ester, fatty acids, surface tension.

INTRODUCTION

Recently a new class of conservation materials is produced, namely - petroleum compositions dissolved in various solvents which, after deposition on metals and evaporation of the solvent, form a film protecting them from corrosion [1]. An important advantage of these materials is their easy deposition on the protected surface, which can be carried out by pulverization or immersion. Different degree of protection can be achieved by regulating the film thickness. These materials are used for internal and external protection of various machines and mechanisms. They penetrate well in microslots and gaps in the protected surface. Higher requirements are posed on the inhibitors present in the compositions, which should protect steel and other metals and alloys from all kinds of corrosion for decades under any conditions. They should also be cheap and easily available or produced from available materials.

Various products of the petroleum refining industry-solid and oxidized hydrocarbons (paraffins, ceresins, petrolatums, vaselines, etc.), polymeric and film-forming substances from other industries like natural rubber, casein, polyolefins, bitumen and latexes, soaps of organic acids and modified silicagels are used as densifiers of these protective coatings [2, 3].

Other important components present in the coatings are the fillers. They can be of quite different type and are usually some solid substance with particle size from 1 to 10 nm. To prevent sedimentation, the fillers are usually accompanied by dispersing agents or surfactants like high molecular mass alcohols, esters, fatty acids, resins, etc.

The plasticizers used play an important role in the formation of a compact uniform layer on the protected surface after evaporating the solvents. They reduce the resistance and hardness of the film but improve its uniformity and elasticity. As a result, the total protection ability of the coating is improved. The mechanism of their action is related to the increase of the mobility of individual molecules. The solvents used to prepare protective coatings should solve all the components or partly solve some of the compounds to form colloid solutions. An important pre-requisite is that the solvents should be volatile and they should not destruct the protective layer by their evaporation. The inhibitors added to the coatings do not differ much from the traditional corrosion inhibitors used for the mineral oils [4 -10].

EXPERIMENTAL

In our previous work [9, 10] experimental design was used to determine the optimum values of temperature, content of the catalyst, content of ethanol, and time of the reaction for the synthesis of the ethyl esters of fatty acids. The process was monitored by determining the acid numbers of the esters obtained according to the ISO 6618 method. The parameters were found to decrease to about 7 - 8 mg KOH/g, which was adopted as completion of the esterification process.

This work is aimed at studying protective coatings for various metal surfaces that can be produced by local industry because of the availability of raw materials and the need for such coatings. In this respect, the present paper offers the preparation of protective compositions on the basis of suitable corrosion inhibitors combined with petroleum oils of different viscosity, densifiers and solvents. It is focused on the following components for the protective compositions: ethyl ester of tall oil fatty acids, ethyl ester of stearic acid and ethyl ester of oleic acid as corrosion inhibitors; paraffin waxes from distillate and residual oil fractions from Bulgarian crude oil, petrolatum and ceresin (densifiers); petroleum oil (plasticizer). All components used were characterized by physicochemical parameters according to the respective standard methods. Table 1 shows

Table 1. Composition of the studied protective coatings.

Corrosion inhibitor, %	Densifier, %	Plasticizer, %	Solvent, %
1	5	90	4
2	10	80	8
3	15	70	12
4	20	60	16
5	25	50	20
10	30	40	20
20	50	20	10

Table 2. Physical-chemical properties of the protective coatings containing corrosion inhibitor ethyl ester of stearic acid.

Properties	Inhibitor, %	Additives				
		Parrafin wax			Petrolatum	Ceresin
		Low-viscosity	Middle-viscosity	Residual		
Time for full drying, h	1	30.2	24.4	27.7	29.1	27.2
	10	71.5	70.2	66.3	80.1	66.1
	20	66.9	50.1	49.2	58.6	48.5
Time for film making, min	1	48	44	39	42	38
	10	124	103	96	104	113
	20	107	96	85	91	84
Colloid stability, % /BDS 6733/	1	90.6	87.6	86.2	80.1	72.9
	10	88.7	85.7	85.3	76.6	71.4
	20	72.7	66.7	58.8	47.8	45.9
Dropping point temperature, ^{o}C /BDS ISO 2176/	1	42.5	48.5	64.0	66.0	71.5
	10	44.5	52.5	69.0	96.0	97.0
	20	44.0	53.5	69.5	98.5	99.0
Relative ohmic resistance, %	1	85	79	77	75	70
	10	93	86	85	82	78
	20	94	90	88	85	82
Surface tension, mN/m /ISO 304/	1	32	29	28	25	24
	10	38	34	32	31	30
	20	40	33	30	29	28
Protective efficiency: - Chamber "Aggressive media", mg "AS" /BDS 14353/	1	2.80	2.71	2.43	2.34	2.30
	10	2.11	2.03	2.00	1.94	1.92
	20	0.97	0.90	0.86	0.80	0.78
- Chamber "Humidity", g/m^2 /BDS 14355/	1	2.44	2.38	2.33	2.20	2.18
	10	1.52	1.41	1.33	1.21	1.17
	20	0.70	0.60	0.55	0.50	0.45
- Chamber "Salty fog", g/m^2 /BDS 14354/	1	50.88	50.41	49.71	48.81	48.31
	10	12.21	11.71	11.20	10.51	10.10
	20	7.41	6.62	6.31	5.52	5.21

Table 3. Physical-chemical properties of the protective coatings containing as corrosion inhibitor ethyl ester of oleic acid.

Properties	Inhibitor %	Additives				
		Parrafin wax			Petrolatum	Ceresin
		Low-viscosity	Middle-viscosity	Residual		
Time for full drying, h	1 10 20	30.1 71.3 66.7	24.2 70.1 49.8	27.4 66.1 49.1	29.0 80.0 58.4	27.1 66.0 48.1
Time for film making, min	1 10 20	47 122 105	42 101 94	38 95 82	41 102 90	37 112 83
Colloid stability, % /BDS 6733/	1 10 20	90.8 88.9 72.8	87.8 85.7 66.9	86.6 85.5 58.7	80.4 76.6 47.7	73.0 71.7 46.1
Dropping point temperature, °C /BDS ISO 2176/	1 10 20	43.0 45.0 44.5	48.5 53.5 54.5	64.5 69.5 71.5	66.5 96.5 99.0	72.5 97.5 99.5
Relative ohmic resistance, %	1 10 20	86 94 95	80 87 91	78 86 89	76 83 86	71 79 83
Surface tension, mN/m /ISO 304/	1 10 20	31 37 39	28 33 32	27 31 29	24 30 28	23 29 28
Protective efficiency: - Chamber “Aggressive media”, mg “AS” /BDS 14353/	1 10 20	2.79 2.10 0.96	2.70 2.01 0.89	2.42 2.00 0.85	2.33 1.91 0.78	2.30 1.91 0.72
- Chamber “Humidity”, g/m^2 /BDS 14355/	1 10 20	2.40 1.50 0.68	2.33 1.38 0.55	2.30 1.30 0.51	2.18 1.11 0.44	2.14 1.15 0.42
- Chamber “Salty fog”, g/m^2 /BDS 14354/	1 10 20	50.74 12.13 7.38	50.28 11.60 6.55	49.57 11.10 6.16	48.66 10.37 5.37	48.21 10.05 5.16

Table 4. Physical-chemical properties of the protective coatings containing as corrosion inhibitor ethyl ester of tall oil fatty acids.

Properties	Inhibitor %	Additives				
		Parrafin			Petrolatum	Ceresin
		Low-viscosity	Middle-viscosity	Residual		
Time for full drying, h	1 10 20	30.0 71.1 66.5	24.1 70.0 49.6	27.1 66.0 49.0	29.1 80.1 58.2	27.0 66.1 48.0
Time for film making, min	1 10 20	46 120 101	40 100 91	36 92 81	40 101 91	35 111 81
Colloid stability, % /BDS 6733/	1 10 20	91.1 89.1 72.9	87.9 85.8 67.2	86.8 85.6 58.9	80.5 76.7 47.8	73.2 71.8 46.2
Temperature of dropping, °C /BDS ISO 2176/	1 10 20	43.5 45.5 45.0	49.5 55.5 55.0	65.5 70.5 72.0	67.0 97.0 99.0	73.5 98.0 100.0
Relative ohmic resistance, %	1 10 20	87 95 96	82 88 93	79 87 90	77 84 87	72 80 85
Surface tension, mN/m /ISO 304/	1 10 20	30 36 38	27 32 31	26 30 28	23 29 27	22 28 26
Protective efficiency: - Chamber “Aggressive media”, mg “AS” /BDS 14353/	1 10 20	2.71 2.06 0.92	2.66 1.93 0.81	2.35 1.91 0.76	2.27 1.84 0.66	2.21 1.77 0.59
- Chamber “Humidity”, g/m^2 /BDS 14355/	1 10 20	2.32 1.44 0.61	2.21 1.27 0.44	2.18 1.19 0.39	2.08 1.09 0.28	2.02 1.02 0.17
- Chamber “Salty fog”, g/m^2 /BDS 14354/	1 10 20	50.67 12.09 7.31	50.06 11.46 6.51	49.51 11.04 6.05	48.55 10.26 5.31	48.11 10.01 5.11

the compositions, which have been subjected to experiments needed to determine their eventual application.

RESULTS AND DISCUSSION

The results from the physicochemical studies of the compositions obtained are presented in Tables 2-4.

The main factor affecting the time for drying the protective coating was found to be the amount of solvent. Its evaporation from the mixture affects the density of the film formed and, therefore - the protection effectiveness.

The contents of plasticizer and solvent are the basic parameters affecting the colloid stability. The amount and type of the densifier has a certain effect on coating contents, as shown by the dropping point temperature.

The ohmic resistance exhibits the ability of the film formed by a given composition to isolate the metal surface from occurrence of electrochemical processes. The values of this parameter depend mainly on the polarity of the components present in the composition. The values of the relative ohmic resistance showed that the density of the protective film depends also on the amount and type of the densifier.

With the increase of the inhibitor concentration (which is actually a surfactant), the surface tension of the protective composition increases and thus affects the size of the drops when spraying it on the metal surface. In the same time, the experiments showed that if the metal parts, which are to be conserved are wet; the water is removed from the surface and incorporated into the protective layer. This is quite important during the conservation process. The increase of the inhibitor content provides possibilities to avoid preliminary treatment and drying of the protected surfaces.

The compositions obtained on the basis of low viscosity paraffin are can be used as conservation oils. They are suitable for conservation of metal parts that have to be stored for long periods of time at higher temperatures. For prolonged conservation under varying temperature, the coating containing ceresin as densifier is assumed to be more suitable. This densifier gives the most stable and dense film. For conservation of moist and wet surfaces, the inhibitor content should be at least higher than 10 %. At lower concentrations the protective compositions do not have good water removing properties.

CONCLUSIONS

Protective coatings were prepared with different corrosion inhibitors – ethyl esters of tall oil fatty acids, ethyl ester of stearic acid and ethyl ester of oleic acid and various by-products from the petroleum refinery.

The physicochemical studies showed that the compositions obtained have good protective properties for metal surfaces.

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