Standard Oil Company
(Indiana)

INFORMATION DIVISION TRANSLATION T46-17

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Study of the Resistance of Different Materials Toward Carbon Monoxide -
July 30, 1943

Purpose: By experiments on CO-corrosion at 250 and 700 atmospheres, attempts are to be made to discover substitute materials for Mn-Cu in apparatus for methanol and the like. The test substances are summarized in appendixes 1 and 2.

Brief Results:

Attacks of CO on massive corrosion samples were carried out in an experimental furnace with a gas mixture CO-H_2 (50%CO) passing through at 250 and 700 atmospheres and with temperatures varying between 170 and 400°. The magnitude of the attack is sharply dependent upon the pressure and (with the exception of a few austenitic materials at 700 atmospheres) shows a decided maximum at 260-300°C. As substitute materials for manganese-copper, at 250 atmospheres, only V2A-extra comes into consideration for the entire temperature range. At temperatures above 350°, on the other hand, all the other materials studied can find application, and at temperatures below 200° all materials with the exception of boiler plate, zinc coated boiler plate and N5. In the case of welded V2A, at 250 atmospheres and 260° no selective attack in the weld seam could be detected.

In order to give a final decision concerning the possible use of these replacement materials, the laboratory tests must be supplemented by a works test.

At 700 atmospheres none of the materials studied can be considered as a replacement for manganese-copper.

Detailed Report

The experiments on CO-attack were continued for the purpose of discovering materials which are suited to replace Mn-Cu partially or completely in the methanol regenerator and furnace. In these experiments the former research method (cf. Analytical Methods report 4144 of April 27, 1942) was abandoned, this is based on the carbonyl formation on filings of the material under examination at a temperature (9MV) considered to be favorable to carbonyl formation, with subsequent decomposition of the carbonyl and deposition of the iron, in an adjacent furnace filled with copper turnings at higher temperature (24 MV), since the results were not reproducible with sufficient exactitude. The newer tests, in which at the same time the most favorable conditions for carbonyl formation are to be determined, were carried out with massive corrosion samples of about 20 x 50 x 4 mm dimensions, which were exposed in a pressure vessel to the action of a current of CO-H_2 gas mixture of 50:50% composition.

With this experimental procedure, results were obtained which agreed well. The tests were made in the laboratory of the Organic Section since gas was not available to us.

The results of these tests, made at 250 and 700 atmospheres and at various temperatures, are summarized on attachments 1 and 2, and represented graphically in attachment 3. The analyses of the materials are shown in attachment 4.

The graphic representation in plate 3 shows that beside manganese copper FF30 and NCT 3 have held up best, and approximately equally. Furthermore that the magnitude but not the temperature range of the CO-attack in the other materials is sharply dependent upon pressure. All non-austenitic materials at 250 atmospheres show a maximum attack at 260°, and at 700 atmospheres at 260-300°. For the austenitic steel V2A-extra, V4A and CF87212, the maximum at 700 atmospheres is evidently shifted to higher temperatures, and at 350° no decrease in the corrosion index is present. The cause of the divergent behavior of these materials has not yet been explained. During the 400° tests of the 700 atmosphere series, in two experiments a portion of the apparatus was cracked, so that the operators who were making the test unfortunately refused to carry out further tests at this temperature. The question of the behavior of the above mentioned materials at 400° must therefore remain open.

From these laboratory tests it is evident that at 250 atmospheres all materials tested can be used above 350°, while below 200° all materials are applicable except boiler plate, zinc-coated boiler plate and N5. For the intermediate temperatures, aside from FF30 and NCT3, only V2A-extra has sufficient resistance. Because of its too great brittleness, FF30 cannot be considered for practical operation, and NCT3 cannot be used on account of too high alloy constituents so that, only V2A-extra has any prospect of finding use as a substitute for manganese-copper. Concerning the actual performance of this material and of those considered for use at temperatures below 200° and above 350°, this laboratory experiment cannot be decisive, only a plant scale test.

Since FF30 and NCT3 are eliminated for the reasons mentioned, none of the materials studied comes into question for use at 700 atmospheres.

To clarify the question of the behavior of the welded V2A the following experiments were made:

In a V2A-extra and a V2A-normal sample, by special heat treatment carbide separation was produced in the grain surfaces such as occurs in the vicinity of a weld seam. These samples and also a specimen of V2A-extra with V2A-cupra welded without previous heat treatment, were exposed at 250 atmospheres and 260° to the CO-attack under conditions similar to those in the previously described tests. In neither the unwelded intentionally granulated V2A nor in the welded sample could any appreciable loss in weight or change in structure due to CO-attack be determined. Figures 1-6 (attachments 5 and 6) show the structure of the specimens after CO-treatment. The repolished unetched plates show that no attack at the grain boundaries has taken place.

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TABLE I

Loss or Gain of Metals in $CO:H_2$ Treatment

250 atmospheres; CO/H_2 = 50/50%; 5 m^3/hr.; 72 hr.
- = loss in mm/year
+ = increase in weight in mg/cm^2

Material	7 mv. 170°C.	9.5mv. 210°C.	12 mv. 260°C.	14.5mv. 300°C.	17.5mv. 350°C.	20.5mv. 400°C.
Copper-Manganese	-0.022	-0.036	-0.002	-0.013	—	—
FF 30	-0.005	-0.002	-0.013	-0.018	-0.008	-0.010
NCT 3	-0.003	-0.004	-0.020	-0.005	-0.007	-0.004
V2A - extra	-0.051	-0.046	-0.071	-0.038	-0.011	-0.012
V4A	-0.007	-0.009	-0.269	-0.107	-0.035	-0.002
V6A	-0.008	-0.005	-0.416	-0.103	+0.005	-0.002
CF67 212	-0.025	-0.036	-0.081	-0.750	-0.037	±0.0
V17F	-0.004	-0.045	-0.858	-0.340	-0.012	-0.007
V13F	-0.010	-0.046	-2.066	-0.445	-0.080	-0.009
V5M	±0.0	-0.049	-1.393	-0.393	-0.033	-0.004
N5	-0.117	-2.54	-2.66	-1.19	+0.109	—
Boiler Plate	-0.546	-11.52	-13.98	-2.39	+0.252	—
Zinc-coated Boiler Plate	-0.088	-0.162	-0.202	-0.103	+0.313	—

TABLE II

Loss or Gain of Metals in $CO:H_2$ Treatment

700 atmospheres; CO/H_2 = 50/50%; 5 m^3/hr.; 72 hr.
- = loss in mm/yr.
+ = increase in weight in mg/cm^2

Material	7 mv. 170°C.	9.5mv. 210°C.	12 mv. 260°C.	14.5mv. 300°C.	17.5mv. 350°C.	20.5 mv. 400°C.
Copper-Manganese	+0.085	+0.206	+0.07	+0.002	—	—
FF 30	-1.004	-0.008	-0.019	±0.0	-0.015	—
NCT 3	-0.003	-0.004	-0.005	±0.0	-0.010	—
V2A - extra	-0.006	-0.088	-0.515	-1.90	-3.86	—
V4A	-0.010	-0.293	-1.49	-1.69	-2.64	—
V6A	-0.044	-0.624	-7.12	-6.81	-0.891	—
CF87 212	-0.023	-0.079	-0.620	-0.857	-4.65	—
V17F	-0.044	-4.91	-7.06	-7.78	-0.607	—
V13F	-0.168	-3.86	-12.87	-8.37	-0.731	—
V5M	-0.150	-3.42	-12.13	-6.91	-0.663	—
N5	-0.122	-4.93	-21.2	-43.4	-0.049	—
Boiler Plate	-2.28	-25.9	-136.8	destroyed	±0.0	—
Zinc-coated Boiler Plate	-0.187	—	-1.31	-1.21	+2.512	—

TABLE III

Chemical Composition of Materials Examined

Material	C	Si	Mn	P	S	Cr	Ni	Mo	Ti	Cu	Fe	Sn
Copper Manganese	—	—	5.1	—	—	—	0.3	—	—	94.1	0.2	0.1
FF 30	0.35	—	—	—	—	30.25	0.20	—	—	—		—
NCT 3	0.09	2.4	0.7	0.023	Tr.	25.2	20.1	—	—	—		—
V2A - extra	0.085	—	—	—	—	18.10	8.75	—	0.27	—		—
V2A - extra*	0.09	—	—	—	—	17.3	8.22	—	0.59	—		—
V2A - normal	0.083	—	—	—	—	17.55	9.30	—	free	—		—
V4A	0.106	—	0.40	—	—	17.5	9.20	2.30	—	—		—
V6A	0.10	0.5	0.34	—	—	17.9	8.9	—	—	2.4		—
CF87 212	0.49	0.63	17.8	—	—	2.89	0.05	—	—	—		—
V17F	0.08	0.60	0.58	—	—	16.2	0.20	—	—	—		—
V13F	0.095	0.35	0.38	0.021	0.006	13.7	0.37	0.34	—	—		—
V5M	0.17	0.46	0.52	—	—	13.9	0.57	0.24	—	—		—
N5	0.12	0.25	0.75	—	—	3.36	0.08	0.30	—	—		—
Boiler Plate	0.09	Tr.	—	0.046	—	—	—	—	—	—		—

* Used for welding experiments.