United States Patent Office 3,586,524
Patented June 22, 1971

3,586,524

CONSOLIDATION OF FORMATIONS BY ELECTROLESS METAL PLATING PROCESS

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No Drawing. Filed July 10, 1969, Ser. No. 840,826
Int. Cl. C23c *3/02;* E21b *33/138*
U.S. Cl. 166—292 7 Claims

ABSTRACT OF THE DISCLOSURE

The method of consolidating incompetent formations at low temperatures in the presence of an electroless basic metal plating solution under conditions of reduced stress by addition to the solution of a small amount of an organic sulfimide.

BACKGROUND OF THE INVENTION

In the U.S. Pats. 3,393,737; 3,438,440; 3,438,441 and pending applications Ser. No. 692,726 filed Dec. 27, 1967 which matured into U.S. Pat. 3,500,926 and Ser. No. 705,907 filed Feb. 16, 1968 which matured into U.S. Pat. 3,500,927 electroless metal plating techniques are described for consolidating unconsolidated formations and it is disclosed that the process provides advantages relative to resin consolidation techniques for consolidating earth formations as described in such papers as J. Pet. Tech. May 1966, p. 545 entitled "Review of Sand Consolidation Experience in Southern Louisiana" J. L. Rike, or J. Pet. Tech. December 1961 paper entitled "Large-Scale Laboratory Investigation of Sand Consolidation Techniques" by W. F. Hoover, or J. Pet. Tech, December 1966, p. 1537 article entitled "Studies of a New Process to Consolidate Oil Sands With Plastics" by B. R. Treadway or as described in U.S. Pats. 3,412,796; 3,419,072; 3,378,071; 3,373,813; 3,310,111; 3,282,338 and the like. In essentially all of these resin consolidation processes for consolidating incompetent formations rigs are required and curing time is difficult to control the resin coating or binding materials are difficult to control relative to temperature changes encountered in the treated formation and these materials also present a water stability problem and are affected by the presence of corrosive acids and the like. This often results in costly operations of restrictive use and benefit and therefore makes the electroless metal consolidation techniques described in the above-mentioned references more attractive since metal consolidated formations require no rig, the formations thus treated are not affected by temperature changes and are water stable and impart high compressive strength to such metallized consolidated formations.

Under low temperature conditions as described in U.S. Pat. 3,438,441, wherein basic electroless metal plating solutions are used to consolidate formations, realitively high plating reaction rates may result in consolidated formations which have a low resistance to stress and are subject to cracking. In this case, when such formations are contacted with hot fluids formation damage results.

It has now been discovered that the addition of a small amount of metal plating solution results in controlled metal deposition and consolidation of formations which are resistant to stress and hot fluid damage. Thus, in consolidating sands or coating materials at substantially normal room temperature, excellent uniform metal coatings are produced by using alkaline-plating solutions containing organic sulfimides such as saccharin.

As indicated, a sulfimide such as saccharin is unique in its capability of providing competent metal coatings where alkaline solutions are used at relatively low temperatures.

However, the metal plating of subterranean earth formations may be used to disperse and implant metal to be used as catalysts, activators, property indicators, etc. In the latter operations it may be advantageous to form deposits which crack and expose large surface areas of metal.

The present invention involves the discovery that in an electroless metal plating at a given temperature the degree of competency of the coating is uniquely responsive to the rate of reaction of the plating solution at the given temperature. This discovery is contrary to what would be expected from the effects from strain-reducing additives in electrolytic metal plating. It can be utilized to form highly competent, or incompetent, coatings at the option of the operator. Moderately cracked coatings can be formed by diluting a solution having a relatively high rate of reaction with a solvent such as 2-ethoxyethanol (Cellosolve), dioxane, glycerol, etc. Highly cracked coatings can be formed by diluting such a solution with a lower alcohol such as isopropanol.

PREFERRED EMBODIMENT OF THE INVENTION

The activator solutions can be any of the activator solutions described in U.S. Pats. 3,393,737; 3,438,440 or 3,438,441 and include stannous chloride and/or palladium chloride solutions which may contain hydrazine and which solutions can be buffered with weak organic acids and their salts. Preferred activator solutions are shown in Tables 1 and 2.

TABLE 1.—COMPOSITION OF ACTIVATOR SOLUTION (A_1)

	Quantity per barrel of solution [1]
Water, gallons	40.7
Gum arabic, gms.[2]	20.6
Hydrazing hydrate (85%), cc.	[3] 256
Palladium chloride solution, cc.[4]	636
$NiSO_4 \cdot 6H_2O$ (Omit when buffers are used.	
90% formic acid or glacial acetic (as needed for pH=4.4) cc.	~160–320
Buffers:	
Formic acid (90%) cc.	640
Sodium formate, pounds	7
Or acetic acid (glacial), liters	6.4
Sodium acetate, pounds	10.5

NOTE: Chemicals must be added to the water in the order listed with complete mixing and dissolving before adding the next chemical.

[1] Contains 10.2 grams $PdCl_2$/bbl. of activator solution.
[2] Requires about 15 minutes to dissolve.
[3] Or 400 cc. of 35% hydrazine.
[4] Contains 1.6 gms. $PdCl_2$, 10 cc. conc. HCl, 90 cc. distilled or deionized water/100 cc. $PdCl_2$ solution.

TABLE 2.—ACTIVATOR SOLUTIONS

(B_1) 900 cc. water
100 cc. of solution comprising
- 919 cc. water
- 81 cc. gum arabic solution containing 0.4/gram/1
- 0.4 cc. hydrazine hydrate (85% solution)
- 1.0 cc. of a solution containing
  - 1.6 grams $PdCl_2 \cdot 2H_2O$
  - 10 cc. conc. HCl
  - 90 cc. water

Add glacial acetic acid to give PH=4.2

The metal plating solutions can also include the compositions described in the above-mentioned patents provided they are modified by the reaction rate modifier and anti-stress and cracking controller of the prevention invention; namely, by the addition of a small amount and sufficient to control reaction rate of an organic sulfimide compound, said compound containing therein at least one radical —SO_2NH. Compounds of this type are represented by saccharin and the alkali metal salts or polyvalent salts thereof such as the sodium or potassium salts of saccharin and their mixtures.

A particularly preferred metal plating solution of this invention is shown in Table 3.

TABLE 3

Composition of low temperature plating solution

Component:	Quantity per barrel of solution
H_2O, gallons	35.9
$NiCl_2 \cdot 6H_2O$, pounds	13.28
$NaH_2PO_2 \cdot H_2O$, pounds	15.95
NH_4Cl, pounds	21.9
30% NH_3, gallons	2.19
Saccharin (O-benzoic sulfimide), pounds	0.5 to 3.505
Or Na Saccharin$\cdot 2H_2O$, pounds	0.5 to 4.61
Solution density, gm./cc.	1.06
Solution pH	8.7

The sulfimide containing metal plating solutions for consolidating earth formations were subjected to the pipe nipple tests which was carried out as follows:

Prepare a sand pack in a pipe nipple 5" long by 1⅜" diameter fitted with appropriate end pieces to retain the sand.

(The sandpack should have a pore volume of about 40 $cm.^3$ for most sands. The inlet volume of the tubing and holder from the pump to the sand inlet face should be about 80 cc. for the system described.) Connect the sandpack to appropriate inlet and outlet tubnig and immersed in a water bath at the desired temperature.

If the sand is oil-free and preferentially water-wet, water may be pumped through the pack to remove any air present. If the sand is non-water-wet or if oil is present, this must be washed out. To accomplish this, flush with 4 or 5 PV each of isopropyl alcohol (IPA), xylene, IPA respectively. The final displacement of IPA with H_2O will provide an oil-free pack in most cases. These washings will be facilitated if all air is first removed by flowing liquid through the pack at atmospheric pressure and at 600 p.s.i. alternatively.

After all air and oil are removed, reduce the outlet pressure to 1 atm. and measure the pressure drop across the sandpack for some convenient water flow rate. The pressure drop will be used to measure any changes in the fluid conductivity of the pack during subsequent operations.

The consolidation test experiment is carried out by passing the various activating and plating solutions through the sandpack under the desired conditions. Finally the pack is flushed with water, which is used to remove all gas as described above. Outlet pressure is reduced to 1 atm. and the inlet pressure measured as before. The difference in the initial pressures (corrected for any differences in flow rate) and the final pressure is used to calculate the loss of permeability in the sandpack. The sandpack is then removed from the bath and opened for inspection and evaluation of the consolidation.

Data from a detailed evaluation of the saccharin system are given in Table 4. It should be noted that most plating times were short in order to produce a weak deposit in which the imperfections could be more closely observed. The "disc" listed in Table 4 was a stainless steel end piece in the inlet of the sand pack. It was found to be very sensitive to stress in that cracking would develop most easily on this member when plated. A coarse sand retaining screen downstream from the disc was less sensitive (generally) and would not show cracking in some cases when the disc did. The 20–40 mesh sand (taking up space at the inlet) was the least sensitive of all and required high stress levels to produce cracking. Thus, observations on these three components gave a good estimate of the stress generated in a given experiment.

TABLE 4.—PIPE NIPPLE EXPERIMENTS

Conditions:
(1) No. 5 Sand (Al-2.0)—600 p.s.i. fluid pressure.
(2) 500 cc. (P¹) colloidal palladium solution for activation.
(3) Spacer and/or plating initiation, if required (see below).
(4) Plating solution (see code number below and composition in Table 5).
(5) Hot water exposure test—500° F. for days indicated.

(A). Miscellaneous—Plating data and observation of cracking:

Run No.	1	2	3	4	5	6	7	8	9	10	11
Spacer	Table 2 (B_1)	H_2O	H_2O	H_2O	B_1	B_1	B_1	B_1	B_1		
Plating solution (Table 5):											
Code	A	B	C	D	E	E	F	E	G	H	I
Key composition	NH_4	SO_4	High citrate	Glycolate				(a)	10% Cellosolve	20% Cellosolve	30% Cellosolve.
° F	90										
F, PV/min. (flow rate)	~0.7		~0.93	~0.77 [b]	~0.72	~0.72	~0.77	~0.84	1.1	1.23	0.70.
N, PV, plating solution	65		~100	80	79	79	83	88	108	150	93.
t, min., plating time	93	78	107	105	110	109	108	105	108	123	137.
Inlet, pH	7.0	8.7	8.8	7.2	7.2	7.2	8.9		8.5		8.4.
Outlet, pH	5.8	8.5	7.9	5.0	5.0	5.0	5.4		7.7	7.8	7.8.
Appearance of inlet:											
Loose solids (trash)	— [c]	—	—	—	—	—	—	—	—	—	None.
Cracking on:											
Disc		Very bad	Very bad			None	Very bad	Very bad	Very bad	Very bad	Very little.
Screen		do	do	None	None	do	do	do	do	None	None.
20–40 mesh sand	Very bad	do	do	N.P [e]	N.P.	do	N.P	do	Some cracks	Few cracks	Trace.
No. 5 sand			do	N.P	N.P	do	N.P	do			

TABLE 4.—Continued

(B). Miscellaneous—Hot water exposure—550° F. and/or observation of cracking

		Hot water exposure		
	Key composition	Days	Comp. str.—p.s.i.[f]	Notes and observations
Run				
1	NH_4F	None		Very badly cracked.
2	$SO_4^=$	do		Very badly cracked—plated at 0 p.s.i. fluid pressure.
3	High citrate	do		Very badly cracked—only ½ enough $(H_2PO_2)^-$ to deplete Ni^{++}.
4	Glycolate	do		Flow too fast for depletion. No plating on inlet 1 cm. of sand.
5	do	6	~0	Most sand dissolved and most Ni plating lost. Metal deposit must not be stable. No plating on inlet 1 cm. of sand.
6	do	11	0	Only thin white shell left of sand. Metal deposit must not be stable. Inlet plated successfully by appearance.
7	do	None		Very badly cracked—high pH must have caused cracking.
8	do	do		Badly cracked (alternate slugs not helpful).
9	10% Cellosolve	4	~200	All sand dissolved leaving Ni shell. Much cracking evident on 20–40 mesh after hot water test.
10	20% Cellosolve	None		20% Cellosolve acts about like 10%. Stress appears to be tensile as usual.
11	30% Cellosolve	2	600	No. 5 sand badly cracked. 30% Cellosolve may be too much as the cracking appeared to be due to compressive stress rather than usual tensile stress.

(C). Saccharin—Plating data and observations of cracking

Run No.	12	13	14	15	16	17	18	19	20	21	22	23	24
Spacer	None	B_1	None	B_1					H_2O				
Plating solution:													
Code number	J	K	L	M	N	O	P	P[1]	J	U	R	S	T.
g./l. saccharin	10			5	10	10	8	0	10	0	4	7	0.
Key composition	U (all Cl^-)		All $SO_2^=$	All $SO_4^=$	SO_4-pH-9.9	SO_4-pH-8.7		Acid	U	U	U	U	U.
° F	90							170	120		~120	120	
F, PV/min. (flow rate)	0.53	0.50	0.64	1.09	1.31	0.67	0.77	~6	1.31	6.2	3.1	1.6	5.3.
N, PV, plating solution	67	121	82	123	106	85	101	77	50	170	164	109	833.
t, min., plating time	127	240	129	112	81	127	133	13	38	28	53	70	158.
Inlet—pH		8.5	8.7	8.9	9.9	8.8				8.7			8.7.
Outlet—pH	7.2	7.1	8.2	8.4	9.6	7.2			7.1	7.8	7.7	7.7	8.4.
Appearance of inlet:													
Loose solids (trash)	Some		Much			None		Much	None	Much			—.
Cracking on:													
Disc	None			Very bad		Some	Increased	None		Very bad		Trace	Very bad.
Screen	do						Some	do		do		None	Do.
20–40 mesh sand	do			Trace	Much	None	None	do		do	None		(g).

(D). Saccharin—Hot water exposure—550° F. and/or observations of cracking

	(h)	Days	Compressive stress after test—p.s.i.[i]	Notes and observations
Run:				
12	[j] 0.53	3	1,000	No cracking or other damage observed.
13	0.50	11	890	20–40 mesh sand gave much cracking but no loss of sand or other consolidation. Deposits showed increased cracking with increased exposure.
17	0.67	2	1,400	Trace of cracking in 20–40 mesh sand. No cracking in No. 5 sand.
18	0.77	2	1,900	20–40 mesh sand badly cracked.
19				This looks like typical acid plating systems which do not degrade in hot water;
20	[k] 1.31			Sample not exposed to hot water (no cracking during plating).
21	6.2	3		Had slightly less cracking than 90° F. plating but still much cracking.
23	1.6	2	2,700	Only trace of cracking evident in 20–40 mesh. Deposits essentially unaffected by hot water.
24	5.3	3	Poor	20–40 mesh badly cracked and little consolidation left.

[a] Alternate slugs of E and U.
[b] Depletion not good, hence values are approximate.
[c] A dash indicates that no observation was made.
[d] Compressive stress by appearance of cracks.
[e] No plating.
[f] From middle of consolidation.
[g] 20–40 mesh was badly cracked after 10 days soaking in water at room temperature.
[h] Flow rate in pore volumes/minute.
[i] From middle of consolidation.
[j] 90° F.—Runs 12 through 18.
[k] 120° F.—Runs 20 through 24.

TABLE 5.—SOLUTION COMPOSITIONS AND CODE

	Solutions listed by code					
	A	B	C	D	E	F
Component, amount:						
H_2O, cc./l	890	725	835	900	870	870
$NiCl_2 \cdot 6H_2O$, grams/l			34.8			
$NiSO_4 \cdot 6H_2O$, grams/l	45	85		37.6	37.3	37.3
$NaH_2PO_2 \cdot H_2O$, grams/l	67	93	34.8	37.6	37.3	37.3
29.4% NH_3, cc./l	74	105	38.2			
NH_4Cl, grams/l			58.0			
$(NH_4)_2SO_4$, grams/l		159				
NH_4FHF, grams/l	56					
Na citrate$\cdot 2H_2O$, grams/l			116			
Na glycolate, grams/l				80.0		
Na succinate$\cdot 6H_2O$, grams/l				37.6	37.3	37.3
70% glycolic acid, cc./l					68.2	68.2
NaOH, grams/l					32.4	38.4
pH	7.0	8.7	8.8	7.2	7.2	8.9
	G	H	I	J	K	
H_2O, cc./l	758	686	600	858	858	
$NiCl_2 \cdot 6H_2O$, grams/l	37.9	30.3	26.6	37.9	37.9	
$NaH_2PO_2H_2O$, grams/l	45.5	36.4	31.9	45.5	45.5	
NH_4Cl, grams/l	62.5	50.0	43.8	62.4	62.4	
29.4% NH_3, cc./l	52.1	41.6	36.5	52.1	52.1	
Cellosolve, cc./l	100	200	300			
Saccharin, grams/l				9.5	10.0	
$(NH_4)_2SO_4$						
pH	8.5		8.4		8.5	
	L	M	N	O	P	
H_2O, cc./l	860	860	827	865	865	
$NiSO_4 \cdot 6H_2O$, grams/l	42.0	42.0	42.0	43.0	43.0	
$NaH_2PO_2 \cdot H_2O$, grams/l	38.0	38.0	38.0	46.3	46.3	
$(NH_4)_2SO_4$, grams/l	79.0	79.0	40.0	80.0	80.0	
29.4% NH_3, cc./l	52.0	52.0	115	53.0	53.0	
Saccharin, grams/l	10		10	10	8.0	
Na Saccharin$\cdot 2H_2O$, grams/l		6.0				
As Saccharin, grams/l		4.5				
pH	8.7	8.9	9.9	8.8		
	P_1	R	S	T	V	
H_2O, cc./l	(1)	858	858	976	858	
$NiCl_2 \cdot 6H_2O$, grams/l	(1)	37.9	37.9	6.3	37.9	
$NaH_2PO_2 \cdot H_2O$, grams/l	(1)	45.5	45.5	7.6	45.5	
NH_4Cl, grams/l		62.4	62.4	72.8	62.5	
29.4% NH_3, cc./l		52.1	52.1	22.0	52.1	
Saccharin, grams/l		4.0	7.0			
pH				8.7	8.5	

[1] 10 g./l. Acetic Acid System (see EPR, 114-67-F).

Saccharin also changes the relative importance of side reactions, giving slightly less H_2 production (not noted in Table 4) and more acid production, which lowers the pH in spent solution (see runs 17 and 18). This effect of saccharin on hydrogen production may indicate that saccharin plays a role in the stress-relieving reaction by causing some H^+ to form (assumed to be a fast reaction) instead of H_2 gas (assumed to be a slow one) from the chemisorbed H_2 on the metal. Also, this may be the mechanism by which saccharin slows down the overall deposition reaction.

The metal plating process of this invention can be modified by any of the methods described in the above patents on the subject as well as in copending applications Ser. No. 850,253 filed Aug. 14, 1969 and Ser. No. 835,-243 filed June 20, 1969 wherein spacer and backflush fluids are employed for this process of consolidating formations.

This invention provides a uniquely advantageous way of avoiding problems encountered in consolidating incompetent subterranean reservoir formations. It is also useful in controlling the competency of substantially any coating deposited by electroless metal plating from an alkaline plating solution on substantially any material. It

is particularly useful where the plating is effected by flowing a plurality of pore volumes of activating and plating solutions through a permeable non-catalytic material, such as a permeable earth formation, a permeable mass and/or structure of plastic, metal, or the like material that is non-catalytic to such a metal deposition, etc. The plating can be effected in order to improve the strength or stability of a granular material and/or an intergranular cementing material within a mass of granular material and/or to plug or reduce the permeability of such a mass or permeable structure, to bond catalytic and/or conductive metal within such a mass or structure, to bond other materials into such a mass or structure, etc.

We claim as our invention:

1. A method of consolidating an incompetent formation comprising treating the formation with an activating solution and thereafter treating the activated formation with a basic metal plating solution containing a small amount of an organic sulfimide until the formation is consolidated into a crack-resistant, water-resistant formation.

2. The method of claim 1 wherein the activating solution is a palladium halide solution and the metal plating solution is a basic nickel halide solution containing saccharin.

3. The method of claim 2 wherein the activating solution is a palladium chloride solution containing a buffering agent and the nickel containing solution is a basic nickel chloride solution.

4. The method of claim 3 wherein between the activator and basic metal plating solutions a spacer fluid is injected into the formation.

5. A method of depositing metal on a solid material comprising contacting the solid material with an activating solution followed by treating said activated solid material with an electroless basic metal plating solution containing a small amount of an organic sulfimide until metal is deposited on the solid material.

6. The method of claim 5 wherein the solid material is a permeable structure composed of non-catalytic material.

7. The method of claim 5 wherein the activating solution is a palladium halide solution and the metal plating solution is a nickel halide solution containing saccharin.

References Cited

UNITED STATES PATENTS

2,513,280	7/1950	Brown	204—49
2,690,402	9/1954	Crehan	117—54X
3,234,031	2/1966	Zirngiebl et al.	106—1
3,417,005	12/1968	Baig	204—49X
3,438,441	4/1969	Richardson	166—292
3,500,927	3/1970	Simpson	166—292

OTHER REFERENCES

Domnikov, Larissa Electroless Nickel Plating from Alkaline Solutions. In Metal Finishing, March 1966, pp. 57–60.

IAN A. CALVERT, Primary Examiner

U.S. Cl. X.R.

106—1; 117—54; 166—300