Further Studies On Plante Plate Formation Using Nitrate As Forming Agent*

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ABSTRACT

Plantè plate formation for stationary lead-acid batteries using nitrate as forming agent has been described. The addition of formic acid and urea along with nitrate in a sulphuric acid bath were reported as suitable in our earlier work. The role of formic acid and urea were re-examined and their addition was found to be having no special advantage.

The loss of formic acid during formation was found to be considerable. Shedding of active material during cycling increased by the addition of urea. Formation using only nitrate as addition agent could give plates which gave capacity as per IS: Sepecification. Shedding was observed to be low during cycling.

30 A.H. plates were formed and their capacities determined. The performance characteristics conformed to the IS; Specification for these plates.

INTRODUCTION

The formation of Plante plate is carried out in sulphuric acid solutions with certain reagents which improve the formation. Perchlorate is usually used in industrial practice and for effective use of same as forming agent, the temperature of electrolyte must be kept low (about 18°C) which would necessitate refrigeration requirements in countries like India. This procedure adds to the cost of manufacture. The forming agent adsorbed by the plate requires thorough washing for its complete removal. Any residual perchlorate deteriorates the plate in use, reducing its service life. Having in view these difficulties, an alternate forming bath containing nitrate as the forming agent had been worked out earlier.[1] In such a bath, formation could be carried out at normal temperatures, the nitrate ions being easily removed by washing. Any residual nitrate ion is also removed by reduction at the cathode on electrolysis during the life of plates. The bath studied earlier had, besides nitrate, addition agents such as urea and formic acid. On a careful analysis of the solution after forming, it was found out that the addition agents nitrate, urea and formic acid, were destroyed during formation. As formic acid is expensive, investigations were further carried out to find out whether some of the reagents could be avoided without impairing the qualities of the formed plates.

EXPERIMENTAL

The formation experiments were carried out with regular Plantè type plates of dimensions 20.5cm x 12 cm specified to give 30 amp-hr at 10 hour rate according to Indian Standards specification. 2.5cm square pieces were cut from the above and used for the investigation. The plates were pretreated for about 1 min. in 1 : 1 nitric acid and washed before taking up for formation.

Formation was carried out under identical conditions using sulphuric acid, formic acid urea and ammonium nitrate in different combinations as shown in Table I. Formation was carried out for 24 hours, 48 hours and 72 hours under each of the conditions shown in Table II to study the effect of duration on formation. 200 ml of each solution in a 250 ml beaker was used and the experiments were carried out at laboratory temperature. Two lead blanks of the same size as the anode were used as cathodes. Fresh solutions and separate anodes were used for each experiment. The composition of the forming baths are given Table I.

The degree of formation was found out by estimating the capacity by discharging the form-

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TABLE I: Composition of the solutions used

Solution No.	1	2	3	4	5	6
Constituents (g/l)						
Sulphuric acid	90	90	90	90	90	90
Ammonium nitrate	..	12	12	12	..	..
Urea	..	..	20	20	..	20
Formic acid	..	..	..	45	45	45

TABLE II: Discharge capacity of plates formed under different conditions

Current density, 15.5 amp/dm² of apparent area; Capacity in ampere-hours.

Duration of forming (hours)	*No. of cycles*	1	2	3	4	5	6
		H_2SO_4	*H_2SO_4 and NH_4NO_3*	*H_2SO_4, NH_4NO_3 and urea*	*H_2SO_4, NH_4NO_3, urea and formic acid*	*H_2SO_4 and HCOOH*	*H_2SO_4, HCOOH and urea*
24	1	Self discharge	0.04	Self discharge	Self discharge	0.17	1.13
	2	0.08	3.28	1.25	1.20	0.40	1.63
	3	0.06	3.75	1.42	1.55	0.37	1.52
	4	0.06	3.00	1.46	1.13	0.33	1.51
	5	0.11	..	1.62	1.76	0.36	..
	6	0.11	2.75	1.45	1.66	0.40	1.40
48	1	Self dishcarge	0.72	2.16	1.53	0.66	1.37
	2	0.13	0.69	3.90	1.88	1.10	1.54
	3	0.30	2.50	3.75	3.75	1.50	2.55
	4	0.30	2.40	3.8	3.86	1.00	3.20
	5	0.30	2.40	3.8	3.75	1.04	3.2
72	1	0.21	1.43	1.5	3.1	0.15	3.45
	2	0.19	1.67	2.2	3.9	0.41	3.6
	3	0.21	1.79	3.2	4.8	0.42	2.00
	4	..	1.69	..	1.95	..	..

ed plates in 1.235 sp. gr. sulphuric acid against formed, fully charged negative plates. Care was taken to see that the positive was limiting the capacity of the cell so assembled for the purpose.

Discharge was carried out at the rate specified in the specification laid down by Indian Standards Institution[2] for such type of plates. The plate was discharged immediately after formation in 1.235 acid and later cycled 4 or 5 times in 1.200 acid, The materials shed during formation as well as during cycling were collected, washed, dried and weighed separately.

Regular 30 amp-hr plates were also formed with only nitrate added to the sulphuric acid solution. The formation was carried out for 24 hours, 48 hours and 72 hours. The discharges of these formed plates were carried out against two box type negative plates in 1.200 acid at laid down in IS Specification.

RESULTS AND DISCUSSION

The capacity obtained from plates formed under different conditions, immediately after formation and also during cycling 5 or 6 times are given in Table II in which is also shown the effect of duration on formation. In Table III, the materials that had shed during forming and during cycling are given respectively, for all the compositions studied. The analysis of the forming solutions is given in Table IV, indicating the consumption of the various addition agents. The capacity at different rates of discharge, of a regular 30 amp-hr plate is graphically represented in Fig. 1.

Effect of duration of formation :

From Tables II and III it can be noted that the duration of formation has a marked effect on the initial capacity obtained and also on the capacity obtained during cycling. The most desired condition would be to get the specified capacity without much of shedding during formation or later cycling. Duration has a pronounced effect on this aspect than the reagents used during forming, as seen from Table II. Formation for 24 hours has given somewhat satisfactory capacity during cycling, which means that during formation sufficient time had not given for the complete conversion of lead sulphate to lead dioxide. Formation with sulphuric acid alone does not give appreciable capacity. From a comparison of the capacity with duration of forming and shedding (Table III), it can be concluded that with nitrate addition, shedding both during formation and cycling put together, remains more or less the same when formed either for 24 hours or for 72 hours. This shows that non-adherent deposit is obtained with nitrate addition which stays on the plate during cycling when formed for 72 hours. Shedding is not disirable during cycling and hence formation for 72 hours with nitrate alone appears to be the best condition.

Effect of the reagents added:

Sulphuric acid alone does not give a layer of lead dioxide which is capable of delivering useful capacity. The reason for this has been explained already as due to formation of a compact film of lead sulphate.

If sulphuric acid, formic acid mixture is taken in the bath and plates are formed for 24 hours or longer, no satisfactory capacity is obtained even though the formation is better than in a bath with sulphuric acid alone. The lead sulphate formed during formation in this solution, perhaps forms a very compact film which does not allow further growth of the film. When urea is added into the bath, it increases formation, as well as the material shed as seen from Tables II and III. The material shed during formation is an indication of the film of lead dioxide being compact or loosely formed.

Urea :

Urea acts in the same way as ammonium nitrate, as is evident from the characteristics of the plates formed in solution 2 and solution 6. But when urea is combined with nitrate as in solution 3, the material shed increases. It can therefore be concluded that when ammonium nitrate is used as forming agent, addition of urea is undesirable. The capacity data of the plates as seen from Table II show that some plates give a lower discharge capacity during cycling than the initial capacity. This can be explained easily on the basis of material shed. The plates which give lower capacity during cycling also show higher weight of material shed during cycling, which is not desirable.

Analysis of addition agents in the bath is given in Table IV. The results show that the addition agents are destroyed during formation and the weight of sulphuric acid left behind depends on the material shed in the form of sulphate of lead. This correlates well with the weight of material shed and the sulphate content of the material shed.

TABLE III: Weight of material shed during forming and cycling

A. During forming (g) *B. During cycling (g)* *C. Total (g)*

Duration of formation (hours)	*Solution No.* 1			2			3			4			5			6		
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
24	0.07	1.02	1.09	3.38	7.0	10.38	2.2	10	12.2	2.3	7	9.3	0.62	0.44	1.06	0.9	8	8.9
72	0.21	0.14	0.35	8.9	2.0	10.9	6.9	21	27.9	8.1	20	28.1	1.88	1.5	3.38	5.75	17.5	23.25

TABLE IV: Analysis of forming solutions

Constituents (g/l)	*Duration of formation (hours)*	*Solution No.* 1	2	3	4	5	6
Sulphuric acid	24	21.5	12.2	9.3	7.7	13.0	10.3
	48	18.8	11.7	10.9	11.1	18.8	11.6
	72	17.0	12.6	11.1	14.5	16.2	11.5
Formic acid	24				0.6	0.8	0.1
Urea	24			Nil	Nil		Nil
Ammonium nitrate	24		Nil	Nil	Nil		

TABLE V: Formation of sulphate without impressing current
Duration of immersion — 20 hours

Solution No.	*Total weight loss of lead (g)*	*$PbSO_4$ retained on the plate* (*g*)	(*% of total*)
1	0.17	0.15	60.0
2	0.82	0.54	44.0
3	0.85	0.39	31.0
4	0.51	0.39	51.5
5	0.51	0.09	12.0
6	0.46	0.27	40.0

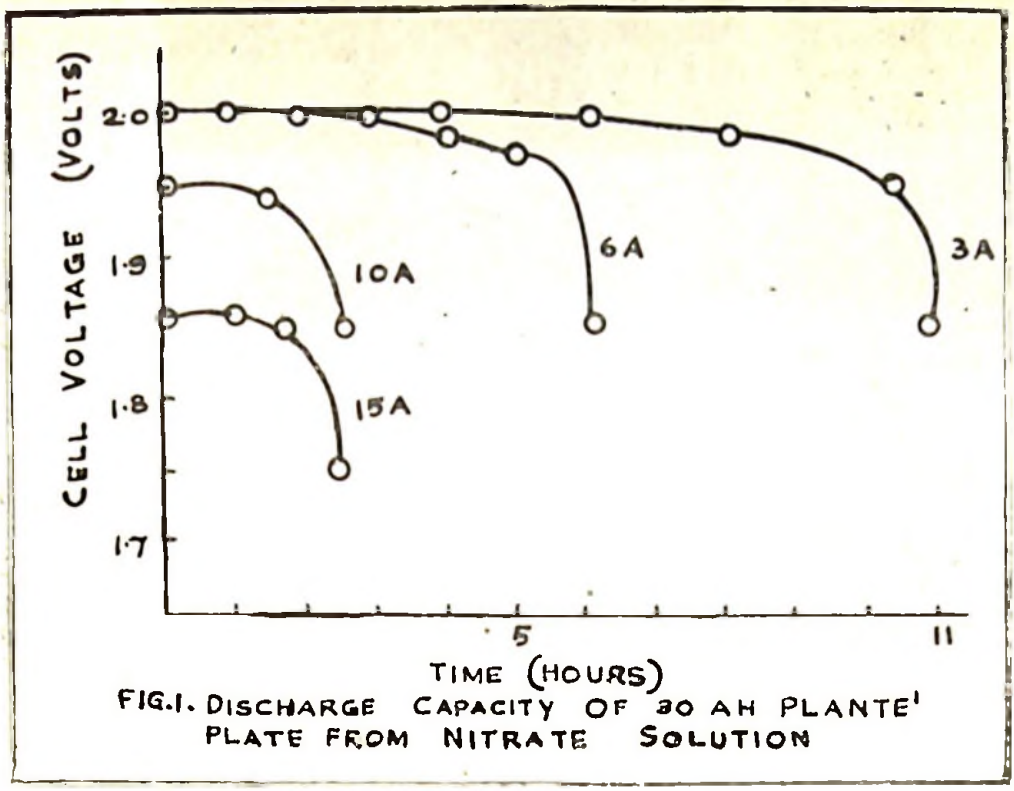


FIG. 1. DISCHARGE CAPACITY OF 30 AH PLANTE' PLATE FROM NITRATE SOLUTION



Fig. 2 : Photograph of plates formed in different solutions :
1 (1), 2 (2), 3 (5), 4 (6), 5 (3), 6 (4), 7 (1), 8 (2), 9 (5), 10 (6), 11 (3), 12 (4)
Numbers given in brackets refer to the No. of solutions given in Table I.

Table V shows the amount of sulphate obtained by keeping the plates of almost equal, surface area in the different forming solution for 20 hours. The weight of sulphate adherent on the plate, roughly indicates the compactness of the film formed and the total weight loss indicates the attacking capacity of the solution on lead. The percentage of sulphate left behind on the plate to the total weight loss shows the same trend as that of the efficiencies of the different solutions.

Fig. 1 represents the discharge capacity of a 30 amp-hr Plante plate at different rates of discharge carried out according to I. S. Specification for such type of plates. It was found that the plates produced by forming in sulphuric acid and nitrate could pass the test satisfactorily. The retention of charge test was also carried out as per the specification. The plates passed this test also.

The photographs of the plates formed in the different solutions are presented in Fig 2. No. 1 to 6 were formed for 72 hours duration and 7 to 12 for 24 hours duration. It can be noted that when the plates are formed for 24 hours, there is a lot of lead sulphate left over on the plates formed in solutions 2, 4, 5 and 6. The attack and formation of lead sulphate is very pronounced in the presence of formic acid. This shows that lead sulphate is first formed and is oxidised further to lead dioxide.

CONCLUSION

From the above experiments, it is evident that

1. formic acid does not serve any useful purpose in the forming solution,

2. urea and nitrate act more or less in the same way when added separately but when combined together in the forming solution, increase the amount of material shed during formation and cycling. Nitrate alone can thus be used as forming agent, as its role is understandable.

3. analysis of the reagents added in the forming bath shows that they are almost completely destroyed during formation. In order to make the process economical, reagents which do not contribute usefully to the process of formation but merely get destroyed during the process can be conveniently eliminated.

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