

Studies on the Production of Magnesium Stearate from Bittern

M. ARSHAD ALI BEG, S. NAEEM MAHMOOD, NAYEEMUDDIN AND M. HABIB

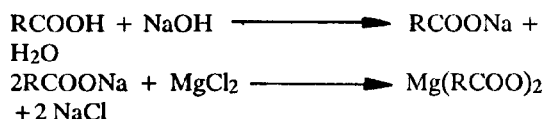
PCSIR Laboratories, Karachi-75280, Pakistan

(Received 12th February, 1991, revised 22nd October, 1991)

Summary: Studies have been carried out to substitute magnesium chloride, a raw material for the manufacturing of magnesium stearate, by bittern which is a waste product of sea salt industry. The prepared metallic soap contains Mg 4.01-4.05%, free fatty acid 0.54-1.02%, and bulk density 0.32-0.41 gm/cc. The product has a reasonable purity (magnesium stearate 98%) and is comparable with the imported metallic soap available in the local market and also with the soaps prepared by using magnesium chloride as a basic raw material by the usual two step method as well as the improved single step method.

Introduction

The metallic soaps are prepared either by precipitation or fusion methods. Precipitation method is preferred for the production of powdered metallic soaps such as stearates, palmitates and rosates of calcium, magnesium, zinc and aluminium [1]. The usual commercial process for the manufacture of magnesium stearate is also a precipitation method. According to this method, a sodium soap is first prepared by saponifying a suitable fatty acid until the latter is neutralized with the requisite quantity of caustic soda, which is reacted in the second step with a solution of magnesium salt to yield the desired metallic soap. The reaction is carried out in two steps which may be represented as follows [2].



Bittern, a locally available waste from sea salt industry has been used in the earlier studies for the production of chemicals viz. magnesium sulphate, magnesium chloride and potassium chloride [3]. The present studies aimed at substitution of magnesium salt with bittern which contains magnesium ions in the form of chloride as well as sulphate and is a resource which needs to be exploited. Experiments reported here comprise utilizing bittern as a basic raw material, by the usual two step process as well as the improved single step method, utilizing magnesium chloride as a raw material. Attempts have also been made to optimize the parameters such as concentration, temperature and time of

reaction and to make preliminary assessment of the factors which affect the purity and quality of the product.

Results and Discussion

Analytical results of the experiment carried out for the preparation of magnesium stearate by the two steps process have been recorded in Table 1. It has been reported that magnesium stearate should not contain less than 3.8% and more than 5.0% magnesium, calculated with reference to the dried product [7]. It would be noted from Table 1 that in the results of almost all the experiments, magnesium when calculated on dry basis was within 3.89 to 4.09%.

It was observed that quality (purity) and yield of the precipitated metallic soap was affected by various factors such as degree of dilution, concentration of reactants, temperature, and rate of stirring etc. However, dilution of the reactants appears to have a significant effect on quality as well as yield of the product. (Tables 1 and 2). Theoretically about 14 gm of NaOH is required to react 100 gm of stearic acid for the preparation of sodium stearate, but 15-20 gm of alkali was utilized to obtain higher yield and complete conversion of 100 gm of acid. It may be noted from Table 1 that in the instances where dilute solutions of NaOH and MgCl₂ were used (Expt. No. 7 to 12), better yield and quality of the product were obtained in comparison to the experiments (Nos. 1 to 6) where relatively concentrated (10 to 20%) solutions were used. However, too much water to dissolve sodium

Table 1: Preparation of magnesium stearate in two steps

Experi- ment No.	1st step (Sod. stearate preparation)			2nd Step (Mg stearate preparation)		% Mg	%Free fatty acid	% Mag- stearate (assay)	% Yield	Bulk density gm/cc.
	Stearic acid	Water	NaOH (conc. & amt.)	Water to dissolve stearate	MgCl ₂ (conc. & amt.)					
1.	105 gm	250 ml	20% soln. (75 ml.)	1,250 ml	20% soln. (200 ml.)	3.95	2.2	95.8	95.2	0.3
2	100 gm	600 ml	15% soln. (100 ml)	2,000 ml	20% soln. (225 ml)	3.89	1.96	94.4	90.5	0.28
3	120 gm	1000 ml	10% soln. (150 ml)	5,000 ml.	20% soln. (250 ml.)	4.0	1.5	97.0	89.8	0.09
4	100 gm.	2000 ml	10% soln. (200 ml.)	4,000 ml.	20% soln. (200 ml.)	3.97	2.7	96.4	94.4	0.11
5	100 gm	2000 ml	10% soln. (200 ml)	1,000 ml	20% soln. (150 ml)	4.0	1.36	97.0	90.0	0.11
6	100 gm.	600 ml	10% soln. (200 ml)	2,000 ml.	20% soln. (200 ml)	3.96	2.03	96.1	96.2	0.22
7	100 gm	1000 ml	5% soln. (310 ml)	2,000 ml	20% soln. (200 ml)	4.01	1.23	97.3	98.4	0.10
8	100 gm	1000 ml	5% soln. (400 ml)	1,500 ml	5% soln. (800 ml)	4.08	1.12	99.0	95.5	0.09
9	100 gm	2500 ml	5% soln. (400 ml)	1,000 ml	10% soln. (400 ml)	4.06	0.82	0.98	98.9	0.1
10	275 gm	4000 ml	5% soln. (900 ml)	1,000 ml	15% soln. (745 ml)	4.04	0.85	98.0	98.8	0.12
11	100 gm	2000 ml	5% soln. (400 ml)	2,000 ml	2.5% soln. (1600 ml)	4.08	0.91	99.0	99.2	0.05
12	180 gm	3000 ml	2% soln. (1800 ml)	1,500 ml	2.5% soln. (2880 ml)	4.09	0.62	99.3	99.0	0.15

stearate (experiments 3 and 4) did not improve the yield and quality of the product. Temperature was also an important factor in this reaction, the optimum range of temperature to carry out this reaction was found to be 70-80°C. It was observed that hot filtration (55-65°C) produced a product with low content of fatty acid. Low temperature produced thick slurries resulting in a relatively high yield but poor quality product having higher bulk density.

A good quality product having lower content of free acid (0.62-0.91%), low bulk density (0.05-0.12 gm/cc) and higher percentage of magnesium stearate (98-99.3%) could be obtained if factors such as dilution, temperature and stirring are appropriately controlled (experiments No. 9 to 12). It was also noted that slow addition of the reactants and thorough mixing with stirring produced good results.

Table 2 summarizes the results of the experiments, carried out to prepare the metallic soap in a single step. It would be observed from the Table that good quality metallic soaps having low content of fatty acid (0.62-0.91%) and low density (0.10-0.12 gm/cc) were obtained when dilute reactants were

used (experiments No. 3 to 8); the yield in these experiments was reasonably good and ranged between 98.5 and 99.0%.

The parameters studied comprised time of reaction, temperature, concentration of reactants as well as the experimental techniques like the sequence of mixing the reactants. In experiments No. 1 to 3 magnesium chloride was dissolved in hot water and solid stearic acid was melted in the hot MgCl₂ solution followed by a dropwise addition of NaOH solution. In experiments No. 4 to 6, stearic acid (solid) was dissolved in the hot solution of NaOH followed by MgCl₂ solution.

The yield and purity of the products obtained from experiments No. 1 to 3 were also comparable to experiments No. 4 to 6, however, it was observed that the products had a relatively higher level of free fatty acid. The temperature in experiments No. 1 to 3 and 4 to 6 ranged between 70 to 80°C and 75 to 85°C respectively throughout the reaction. The time of mixing of the reactants in experiments No. 1 to 3 range from 40 to 60 minutes. In experiments No. 7 and 8, the experimental conditions were similar to that of No. 4 to 6 but more dilute solutions were used and the reactants were added slow-

Table 2: Preparation of magnesium stearate in single step

Experi- ment	Stearic acid	MgCl ₂ (conc. & amt.)	NaOH (conc. & amt.)	Yield (conc. & amt.)	Mg (conc. & amt.)	Free % acid %	Magne- % stearate (assay) %	Bulk fatty gm/cc	sium	density
1	104 gm	2.7%(1500 ml)		22% (91 ml)		97.2	4.01	1.12	97.8	0.15
2	105 gm	2.5 %(1600 ml)		20% (100 ml)		97.1	4.03	1.09	98.2	0.16
3	100 gm	2.5%(1600 ml)		5% (400 ml)		98.0	4.07	1.06	98.8	0.12
4	295 gm	2.5%(4800 ml)		5.4%(100 ml)		97.9	4.06	0.82	98.5	0.12
5	100 gm	2.2%(1800 ml)		5% (400 ml)		97.2	4.07	0.83	98.8	0.10
6	180 gm	2.6%(2800 ml)		4% (876 ml)		97.5	4.06	0.75	98.5	0.11
7	180 gm	2.4%(300 ml)		3.5%(100 ml)		97.8	4.08	0.62	99.0	0.10
8	180 gm	2.5%(2880 ml)		2% (1750 ml)		97.6	4.07	0.64	98.8	0.11

ly (60 to 80 minutes) while mixing thoroughly. It was noted that the slow addition of the reactants provided sufficient time for completion of the reactants resulting in the better yield and purity of the end product (experiments No. 7 and 8)..

In the single step method there is saving of both time and energy which increases the capacity and reduces the manufacturing cost.

Bittern, the waste product of the sea salt industry has been used for manufacturing the salts of magnesium, calcium and potassium [8- 11] but a survey of the literature revealed that it has not been utilized for the production of metallic soaps. The results of the experiments utilizing bittern as a substitute of magnesium salts have been recorded in Table 3. It would be noted from the Table that a product of reasonable purity could be prepared from bittern. The physico-chemical analysis of the products obtained is: Mg 4.01-4.05%, free fatty acid 0.54-1.02%, bulk density 0.32-0.41 gm/cc, and magnesium stearate 94.66-98.06%. The melting point and ash content range from 95.5 to 140°C and 7.1 to 8.4% respectively. The product is comparable with the metallic soaps which have been prepared using magnesium chloride as a basic raw material (Tables 1 and 2). It is also comparable with the imported metallic soap available in the local market. The physico-chemical analysis of the imported product is: Mg 4.55%, free fatty acid 1.3%, bulk density 0.18 gm/cc, m.p. 145°C and ash 6.57%. The slightly higher bulk density of the stearate from the bittern is possibly due to the presence of sodium impurity. The higher concentration of salt in the sea bittern (NaCl 11.05%) have slightly affected the quality and yield of the product. Magnesium is present in the bittern as MgCl₂ (8.1%) and MgSO₄ (6.2%) and usually the salt which is used for the production of magnesium stearate is either magnesium sul-

phate or magnesium chloride because both react easily with sodium stearate. Hence both the major constituents of the bittern are utilized in the reaction making bittern an inexpensive and suitable material. The main difficulty in using bittern as a substitute of magnesium salt seems to be the variation in the concentration of magnesium during different seasons [14].

The salinity of the locally available sea bittern varies from 27 to 31% and its chemical composition is very sensitive to the changes in temperature, humidity, wind velocity and its direction and it is very difficult to get a product of identical composition for a given density [12]. However, this difficulty can be overcome by concentrating the bittern by solar evaporation to a density of 1.31 to 1.32 gm/cc which could be diluted to a required magnesium ion content.

The experiments carried out during this study have established that bittern may be used in the process as a substitute for magnesium salts. The average annual production of bittern from various salt works in and around Karachi is of the tune of 50,000 tons [13] which at present is dumped back into process stream causing deterioration of the quality of solar salt. The utilization of bittern would provide an inexpensive source of the magnesium salts as well as help cure the sickening sea salt industry of the country. However, further investigations regarding the use of sea bittern for the production of magnesium stearate have obviously been indicated by the present studies.

On the basis of the observations made during the experiments, it may be concluded that the properties of the precipitated metallic soap are mostly affected by the factors such as purity of the raw materials, concentration of the reactants,

Table 3: Magnesium stearate from bittern.

Experiment No.	1st Step (Sodium stearate)			2nd Step (Magnesium stearate)			% Yield	%Mg	%F.F. Acid	%Mg stearate (assay)	Bulk density gm/cc
	Stearic acid	Water	Sodium Hydroxide (conc.& amt)	Water to dissolved sodium stearate	Bittern 30°Be	Diluted to					
1.	100 gm	500 ml	3.6% (500 ml)	1 lit.	100 ml	600 ml.	94.4	4.01	1.02	97.33	0.38
2.	100 gm	2000 ml	5% (400 ml)	1 lit.	100 ml.	800 ml.	96.2	4.02	0.93	98.06	0.41
3.	100 gm	900 ml	5% (360 ml.)	0.5 lit.	100 ml	1000 ml	96.6	4.04	0.62	94.66	0.36
4.	100 gm	900 ml	5% (310 ml)	0.8 lit	100 ml	1000 ml	96.1	4.05	0.54	95.8	0.32
5.	100 gm	1000 ml	4% (500 ml)	1 lit	100 ml.	500 ml.	93.5	4.02	0.85	97.87	0.33
6.	100 gm	800 ml	4.5% (450 ml)	1 lit.	100 ml	700 ml	95.5	4.03	0.82	97.52	0.35

temperature of the reacting solutions and rate of mixing of the reactants. Particularly the degree of dilution has a significant effect on the bulk density and purity of the precipitated product. Factors such as precipitation conditions, washing and drying must also be carefully controlled to get a final product of the requisite quality. Since the reaction is the double decomposition of the reactants, soluble salts such as sodium chloride and sodium sulphate are produced which ultimately form the impurities of the metallic soap. The impurities have to be removed to improve the quality of the product by repeated washings. It has been observed that 100 gm of the product requires about 1000 ml of potable/tap water and 100 ml of distilled water to get rid of the soluble impurities. The pure washed material from which most of the water has been removed is dried carefully. Unnecessary prolonged drying should be avoided because owing to its essentially organic nature and extremely large surface area there is a risk of partial diffusion and oxidation.

Experimental

Bench scale experiments were carried out utilizing commercial magnesium chloride (95.7%), stearic acid (92.8%) and caustic soda (82.8%). Stearic acid was melted in a container containing hot water (75-80°C) and fitted with a speed controlled stirrer. Due care was taken to maintain the temperature of the contents of the vessel above the melting point of the stearic acid (60°C). The stearic acid melt was reacted with a dilute solution of caus-

tic soda which was added dropwise, using phenolphthalein indicator to check the completion of the reaction. A slight excess of caustic soda was added to ensure complete conversion of the acid. The sodium stearate thus formed was in the form of a thick paste which was diluted by water while stirring the contents of the vessel and maintaining a temperature between 75-80°C. When solution/slurry of the desired composition was formed, a dilute solution of magnesium chloride, containing stoichiometric quantity of magnesium ions, was added to the hot solution of sodium stearate to precipitate out the magnesium stearate. Stirring was continued for some additional time even after the addition of aliquot magnesium chloride solution, maintaining a temperature of 75-80°C throughout the reaction. On completion of the reaction, the hot slurry was filtered off (centrifuged) and washed successively with tap water and distilled water to get rid of the impurities. The product thus obtained was dried in the hot air and ground to give a uniform particle size most of which could pass through 200 mesh.

In the single step process, stoichiometric amount of magnesium chloride was dissolved in water at 70-75°C and the requisite amount of stearic acid was added to the hot solution, followed by slow addition of the caustic soda solution. After addition of the aliquot caustic soda solution, temperature was raised to about 85°C and stirring was continued for about 30 minutes. Filtration, drying and grinding were carried out as stated earlier.

In the process utilizing bittern for the production of magnesium stearate, metal salt viz. magnesium chloride has been substituted by the sea bittern (30°Be) having an average composition; NaCl 11.05%, KCl 1.7%, MgCl_2 8.1% and MgSO_4 6.2% (percent by weight).

The process was carried out in two steps as detailed previously; the only difference being that in the second step a dilute solution of bittern (1:5) was added dropwise in place of magnesium salt to the hot sodium stearate solution to precipitate magnesium stearate.

The assay of magnesium stearate was determined by titrating acidic solution of the metallic soap with 0.1N NaOH [4]. Magnesium was estimated by complexometric method, titrating alcoholic solution of the magnesium stearate with 0.01 M EDTA solution employing methyl blue indicator [5]. Free fatty acid was determined by titrating acetone/alcohol extract of the metallic soap with 0.05 NaOH and also by acetone extraction method [6].

References

1. J. Matliello, Joseph, Protection and Decorative Coating (John Wiley and Sons Inc., New York, 1947), Vol. II, pp. 615, 619.
2. E.K. Raymond and F.O. Donald, Encyclopaedia of Chemical Technology (The Interscience Encyclopaedia Inc., New York, 1950) Vol. 5, pp 209.
3. M.A.A. Beg, Nayeemuddin and S.N. Mahmood, *Pak.J.Sci.Ind.Res.*, 29(5), 389 (1986).
4. The United States Pharmacopoeia (U.S. Pharmacopoeia Convention Inc., New York, 1965) XVII Revision, pp. 349.
5. T.A. Kiss, O. I. Knezevic, *Microchem. J* 13(3), 459 (1968).
6. S.B. Elliot, The Alkaline Earth and Heavy Metal Soaps (Reinhold Publishing Company, New York, 1946), pp. 278.
7. British Pharmacopoeia (Her Majesty's Stationery Office, London, 1980) Vol. 1, pp. 266.
8. G.T. Gadre, A.V. Rao and H.M. Bhavanagry, *J.Sci.Ind.Res. (India) D 17A*, 141 (1958).
9. P. Hadzeriga, Recovery of values from Natural Lake and Sea Brines, U.S. Patent 3099, 528, 1963.
10. J.B. Butt, J.A. Tallmadge and H.R. Savage, *Chem.Eng.Process* 60, 50 (1964).
11. K. Seshdadri, J.F. Bhat, C.G. Davi and J.R. Sanghavi, *Salt. Res. and Ind.*, 7, 39 (1970).
12. M.A.A.Beg, Nayeemuddin and S.N. Mahmood, An Overview of the sea salt industry in Pakistan, International Symposium on salt and Marine Chemicals Research, Bhavangar, India (1982).
13. M.A.A. Beg, S.N. Mahmood and Nayeemuddin, *Pak. J.Sci.Ind. Res.* 29(4), 301 (1986).
14. M.A.A.Beg, S. Naeem Mahmood and Nayeemuddin, *Pak.J.Sci.Ind.Res.* 32(2), 126 (1989).