

UNITED STATES PATENT OFFICE

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SALT PRODUCT

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This invention relates to a hygroscopic salt which will remain free-flowing and will not cake although kept for long periods under moist, humid conditions. Hence the invention is particularly applicable to common table salt (sodium chloride), but is advantageous in practically all cases where it is desired to use sodium chloride or other hygroscopic salts in flowable form. For convenience the invention will be described hereinafter with reference to table salt.

It is common experience that table salt exposed to a humid atmosphere absorbs moisture rapidly and soon becomes unfit for table use, whether kept in shakers or other receptacles on the table or in open canisters on the shelf. As its moisture content increases, the salt becomes damp and loses its normal flowability so that it can not be spread or distributed evenly, in which condition it will also clog shaker openings and will not shake out at all. If the moisture content is of a sufficiently high level, the salt, on subsequent drying, agglomerates into hard lumps or cakes that can be broken up only with great difficulty. Both of these effects are very troublesome and in an effort to minimize them it is customary among manufacturers to blend (i. e., mix) a small amount of an inert conditioning agent or filler such as tricalcium phosphate with the salt. These agents, in the form of a fine powder, are distributed by blending over the surfaces of the salt particles and thus tend to minimize the sticking together of the salt particles which would result in loss of flowability and eventually in caking. Other inert conditioning agents have been proposed for the same purpose, such as calcium carbonate, magnesium carbonate, silica gel, etc. Such agents are helpful in maintaining the salt longer in flowable condition, but are by no means a satisfactory solution of the problem as shown by everyday experience.

On the other hand, it has been proposed for the same purpose to blend the hygroscopic salt with insoluble metal soaps such as metal stearates which are water-repellent. However, such soaps have never been used in practice as far as we are aware. When salt blended therewith is shaken or otherwise spread over the surface of a liquid, it tends to float in a layer on the surface and vigorous agitation is necessary to effect dispersion. As the salt itself dissolves, the water-repellent soap particles separate therefrom and collect on the surface of the liquid, forming an unsightly scum. Also such salt blends tend to ball up when placed in water or

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like liquid. These objectionable effects are quite apparent even though the amount of metal soap is reduced to a few tenths of one per cent of the salt. They become less apparent as the amount of metal soap is further reduced and are perhaps not material at very low concentrations, but the effectiveness of the soap is reduced correspondingly and at such low concentrations the soap provides no significant improvement in the flowability and resistance to caking of the salt.

One of the objects of the present invention is to provide a salt which is far superior in flowability and caking resistance to any prior commercial salt with which we are familiar.

Another object is to eliminate the disadvantages mentioned above which have heretofore militated against if not prevented the use of insoluble metal soaps.

Further objects are to accomplish the foregoing results without impairing the flavor or quality of the salt and without unduly increasing its cost.

We have found that the heretofore mentioned objections to the use of water-repellent insoluble metal soaps can largely be avoided if the soap is caused to adhere to or coat the salt particles as described hereinafter. Also the adhering soap is more effective in maintaining flowability and preventing caking of the salt than soap which is merely mixed with or dusted on the salt. On the other hand, the adhering soap renders the salt particles more difficultly soluble and if the amount of soap is sufficient to effect significant improvement in the flowability and anti-caking properties of the salt, then prolonged stirring is necessary in order to disperse the insoluble soap before the salt itself will dissolve. However, we have found that this further difficulty can be avoided by the use of a surface-active agent which assists in dispersing and solubilizing the soap. Thus it is possible to use the treated salt in the normal manner without scum and without inconvenience due to slow dissolution.

In using insoluble metal soaps in the above manner, we have observed that they are somewhat less effective in maintaining flowability than in preventing caking. A small amount of soap appears to repel part of the moisture to the surface of the bed of salt so that if caking should occur on subsequent drying, the cake is restricted to a relatively thin surface layer of the bed and can be broken up easily. However, some moisture is absorbed throughout the mass of salt so that it soon reaches the moisture level at which

it becomes non-flowable. Hence a relatively large amount of soap must be used to produce substantial improvement in flowability whereas as much smaller amount will produce a high degree of improvement in anti-caking properties.

On the other hand, inert conditioning agents such as those mentioned above are more effective in maintaining flowability than in preventing caking, being relatively ineffective in the latter respect as compared with insoluble metal soap. Hence we prefer in practice to employ both an inert conditioning agent and an insoluble metal soap in combination. As the absorption of moisture by the salt progresses, flowability is maintained by the conjoint action of these agents a large part of which is attributable to the inert conditioning agent. Anti-caking properties are also contributed by both agents, but the part played by the soap is relatively much greater and that played by the inert conditioning agent is relatively much less than in the case of flowability. Hence the amount of soap is determined principally by the degree of improvement in anti-caking properties that is desired, whereas a high degree of improvement in flowability is obtained at the same time due to the greater effectiveness of the inert conditioning agent in this respect. This conjoint action thus permits a reduction in the amount of soap required and reduces the cost of the final product since such soaps are normally more expensive than suitable inert conditioning agents. However, it will be understood that soap and surface-active agent can be used without the inert conditioning agent if desired.

In general, any water-repellent metal soap can be employed, as for example, soaps of the alkaline earth metals, of aluminum, lithium, etc., with any of the various higher fatty acids such as stearic, palmitic, lauric, behenic, etc. However, the effectiveness of such soaps for the purposes of the invention varies, and also some of them may require different treatments than others to cause them to adhere to the salt. The method which is preferred for simplicity and cheapness and for effectiveness as well is to blend or mix the soap with the salt and then to heat the mixture to the softening point of the soap to cause it to adhere to the salt on cooling. For best results the soap should be finely divided in the form of an impalpable powder. Where the above method is not feasible, however, other suitable methods may be used such as dissolving the soap in a volatile solvent and spraying or otherwise distributing the solution on the salt. Prolonged working of a dry mixture of salt and soap to achieve a spreading or coating of the soap on the salt also is effective, particularly if the salt is warm.

The amount of soap to be used will depend on the degree of improvement that is desired in the properties of the salt, on the degree of effectiveness of the particular metal soap used, and of course on whether or not an inert conditioning agent is employed as well as soap. By way of example, particularly effective soaps such as magnesium, calcium, and lithium stearates may be used in very small amounts of the order of 0.2-0.3% by weight of the salt, in combination with inert conditioning agents such as magnesium carbonate in amounts of 2-3% on the same basis, with the result that the salt remains flowable several times as long as the untreated salt and resists caking even more. Lesser amounts of these soaps and conditioning agent can be used,

but at the sacrifice of some of the protection afforded the salt. As a rule it will not be desirable to reduce the amount of soap below about 0.05% or the amount of conditioning agent below about 0.25%, because the degree of improvement in the properties of the salt would then become unimportant. Larger amounts of the soap and conditioning agent, on the other hand, provide still greater protection than that mentioned above, but generally it is undesirable for the amount of the combined ingredients to exceed about 5-6% of the salt because solutions of the latter then tend to become cloudy and turbid. Within this practical limit, the proportions of soap and conditioning agent may vary. Both may be increased more or less proportionately to say 0.5-1% soap and 4.5-5% conditioning agent, or one only may be increased as for example in the case of 0.2-0.3% soap and 5% conditioning agent, etc.

The amounts of other soaps to be used will differ somewhat from the amount of magnesium stearate for the same degree of improvement in the properties of the salt. Calcium and lithium stearates, for example, are practically as effective as magnesium stearate and can be used in approximately the same amounts whereas aluminum stearate is less effective and must therefore be employed in greater amounts. The amount of soap required may also be influenced to some extent by the use of conditioning agents other than magnesium carbonate as described hereinafter.

If no inert conditioning agent is used, on the other hand, the amount of soap needs to be largely increased if substantial improvement in flowability is to be effected. With magnesium stearate, for example, the amount of soap needs to be increased to about 2% to effect as much improvement in flowability as the combination of only 0.2-0.3% magnesium stearate plus 2% magnesium carbonate. However, the cost of such increased amount of soap is several times that of the much smaller amount of soap plus the conditioning agent. Hence it is not desirable as a general rule to use soap without conditioning agent, the conjoint use of less soap together with a conditioning agent being preferred because of greatly reduced cost.

Generally speaking, the inert conditioning agent may be of any suitable kind such as those mentioned above, but we have found that such agents vary in effectiveness. Magnesium carbonate is one of the most effective conditioning agents and in practice we prefer to employ about 2% magnesium carbonate by weight of the salt. As the amount of magnesium carbonate is decreased, flowability is lost at lower moisture levels and therefore more quickly, and below about 0.25% the conditioning effect of the magnesium carbonate becomes unimportant from the practical standpoint. On the other hand, the amount of magnesium carbonate can be substantially increased up to 4.5% for prolonged flowability as noted above.

Similar variations may occur in the amounts of other conditioning agents which in general are less effective than magnesium carbonate. For example, nearly twice as much tri-calcium phosphate is required to maintain flowability to the same extent as with magnesium carbonate. Hence within the practical upper limit of around 5% conditioning agent mentioned above, substantial improvement in flowability can be effected with conditioning agents other than mag-

nesium carbonate, but the latter is more effective at much lower concentrations.

Any suitable method may be employed for adding the conditioning agent to the salt. However, these agents being in the form of dry dust or powder are preferably simply mixed thoroughly with the salt by stirring or the like.

The primary requirement for the surface-acting agent in all cases is the ability to aid in the wetting and dispersion of the soap. However, in table salt the surface-active agent should preferably impart no objectional flavor to the salt or to products seasoned therewith, and should not produce toxic or otherwise objectionable thermal decomposition products when subjected to maximum cooking temperatures, say 500° F.-600° F. These requirements lead to the following types and classes of surface-active agents:

- I. Anionic agents of the class of sulphonated amides such as the commercial products "Igepon T," "Sintex T," and "Hytergron," for example.
- II. Cationic agents of the following classes:
 - A. Substituted ammonium compounds such as cetyl dimethyl benzyl ammonium chloride and the commercial products "Onyxsan S" and "Quatronyx," for example.
 - B. Cyclic quaternary ammonium compounds such as the commercial products "Hyamine 1622," "Hyamine 100" and "Alrosett," for example.
- III. Non-ionic agents of the following classes:
 - A. Polyethylene glycol fatty acid esters such as the commercial products "Polyethylene Glycol 600 Monostearate," "Polyethylene Glycol 600 Distearate" and "Polyethylene Glycol 600 Tristearate," for example.
 - B. Ethers including
 1. Alkyl aryl polyether alcohols, for example, the commercial products "Triton X-100" and "Triton X-30."
 2. Polyalkylene derivatives of hexitol anhydride fatty acid esters such as polyoxyethylene sorbitan monolaurate and the commercial products "Atlas G7596B" and "Atlas G7596C," for example.

The surface-active agent can be applied to the salt in any suitable manner, whereby it is distributed with reasonable uniformity throughout the mass of salt. For example, it can be dissolved in a suitable solvent which is distributed over the salt and the solvent then allowed to evaporate. The surface-active agent can also be absorbed on the conditioning agent, when used, and the mixture then blended with the salt, but in such cases an excess amount of surface-active agent is desirable because some of the agent may not be released for action in dispersing the soap. The preferred method, however, is to mix the surface-active agent with a small quantity of salt which mixture is then blended with a larger quantity of salt to obtain the desired distribution of the surface-active agent. For example, Hyamine 1622, a solid, can be mixed thoroughly in finely divided form with a small quantity of salt, providing a mixture which can be blended conveniently with the major portion of the salt. Similarly polyethylene glycol 600 distearate, which is a waxy solid, can be ground with a small quantity of salt, and polyoxyethylene sorbitan monolaurate, which is a viscous liquid, can be mixed thoroughly with a small quantity of salt, to provide mixtures for subsequent blending with the major portion of the salt.

The amount of surface-active agent to be used depends in the first instance on the wetting and solubilizing capacity of the particular agent employed and on the rapidity with which the salt is desired to disperse and pass into solution, but the effect of the agent on the dry mixture of salt is also a factor. If the amount of surface-active agent is too small the salt will be difficult to

disperse and dissolve. If the amount of surface-active agent is too large the salt will disperse and dissolve readily enough but will tend to become damp and non-flowable on exposure. However, this tendency may be counteracted and the advantage of rapid dispersion still obtained by suitable additions of inert conditioning agent.

For most purposes, it will be found desirable to use an amount of surface-active agent which will cause the treated salt to disperse and dissolve with a readiness as nearly comparable to that of plain salt as practicable and yet not become non-flowable on exposure. However, there may be occasions when, in the interest of assuring particularly good flowability, a lower degree of dispersibility than otherwise attainable may be preferred and, conversely, a higher rate of dispersion may at times be desired at the sacrifice of flowability. Moreover, the presence or absence of an inert conditioning agent, as well as the soap content of the salt when no filler is used, will have a bearing on the extent to which the dispersibility of plain salt can be approximated by addition of a surface-active agent without rendering the treated salt non-flowable. Thus, a greater amount of surface-active agent can safely be used when a conditioning agent is present, and salt having no filler but a high soap content will tolerate more of the surface-active agent without becoming non-flowable than salt having a low soap content. In any event, the safe upper limit on surface-active agent addition will be about the same whether the salt contains an appropriate amount of conditioning agent or its equivalent in the form of a higher proportion of soap.

The actual amount of surface-active agent required in a given case will of course depend on the effectiveness of the particular agent used. With polyoxyethylene sorbitan monolaurate and Hyamine 1622, for instance, the addition of as little as 0.025% by weight of the salt may be sufficient when only a small improvement in dispersibility is desired, whereas use of 0.1-0.2% will impart a rate of dispersion and dissolution approximating that of plain salt but result in a non-flowable product unless the salt is blended with a suitable quantity of conditioning agent or has a soap content of equivalent value. On the other hand, if Igepon T or polyethylene glycol 600 distearate is used as the surface-active agent, considerably larger amounts may be employed to improve dispersibility before encountering any problem of non-flowability. With them, as much as 0.5% may safely be incorporated in salt having a low soap content, and as much as 0.75% in salt containing an added conditioning agent. Similar variations in effectiveness may be expected with other surface-active agents of the types heretofore named, but in general the proportions in which they will be found useful will fall within the limits above mentioned.

By way of example, a suitable table salt may be prepared in the following way. Hot salt as it comes from the screens (about 175° F.) is first blended with 0.25% finely powdered magnesium stearate, after which the temperature of the blend is raised to about 160° C. The stearate softens and melts partially at this temperature, creeping over the surfaces of the salt particles and adhering firmly thereto on subsequent cooling. A small part of this salt, say 5%, is then mixed with an amount of polyoxyethylene sorbitan monolaurate equivalent to 0.15% of the whole, and this mixture is then blended with the remainder of the salt. Finally the so-treated salt

is blended with about 2% magnesium carbonate.

A blend prepared in the above manner was compared with a blend of the same salt with the same amount of magnesium carbonate only. A quick practical comparison as to flowability can be made by adding known volumes of water to the samples and determining the moisture levels at which the salt will no longer shake from shakers. Both samples became non-usable at about 1.75% moisture, since the amount of soap was small and flowability was maintained principally by the magnesium carbonate. However, the flowability of the first sample embodying the present invention was better as the moisture level approached this limit, as shown by the fact that at 1.25% moisture only 2% of the first sample remained in the shaker as compared with 28% of the second sample under the same conditions.

The use of the same amount of soap but of increasing amounts of magnesium carbonate up to 5% raised the moisture level at which the salt became non-usable to 4.75%. When the soap was omitted, the salt plus 5% magnesium carbonate alone became non-usable at 3.5% moisture, the effect of the soap on flowability being more evident under these conditions.

The effect of the soap on anti-caking properties was much more marked. The second sample (2% $MgCO_3$ on'y) was 87% caked in the shaker after being kept in a bell jar over water for 96 hours and then dried 16 hours at 45° C., whereas the first sample (including 0.25% soap) was only about 8% caked after 168 hours exposure and only 45% caked after 240 hours exposure in the bell jar. Both samples were far superior to the untreated salt which was 72.5% caked after only 48.5 hours in the bell jar.

In the absence of magnesium carbonate, the amount of soap had to be increased to about 2% to provide approximately the same flowability as in the above example, in which case anti-caking properties were somewhat better than in the example. Soap concentrations of 1% provided substantially the same anti-caking properties as in the above example, but somewhat poorer flowability although still superior to the untreated salt.

All of these samples embodying the combination of soap and surface-active agent did not form scum or ball up when added to water, and dissolved readily without stirring.

It will be understood that the above specific examples are for purposes of illustration only and that other amounts and proportions of soap, surface-active agent, and conditioning agent, as well as other species of these agents, may be employed without departing from the spirit of the invention. Reference should therefore be had to the appended claims for a definition of the limits of the invention.

What is claimed is:

1. A free-flowing, non-caking salt composition consisting essentially of a normally hygroscopic salt having a water-repellent metal soap adhering to the particles thereof, and a surface-active agent of the group consisting of sulphonated amides, substituted ammonium compounds, cyclic quaternary ammonium compounds, polyethylene glycol fatty acid esters, alkyl aryl polyether alcohols and polyalkylene derivatives of hexitol anhydride fatty acid esters, the proportions of soap and surface-active agent being about 0.05-2.0% and 0.025-0.75%, respectively, of the weight of the salt.

2. A free-flowing, non-caking salt composition

consisting essentially of a normally hygroscopic salt having a water-repellent metal soap adhering to the particles thereof, a surface-active agent of the group consisting of sulphonated amides, substituted ammonium compounds, cyclic quaternary ammonium compounds, polyethylene glycol fatty acid esters, alkyl aryl polyether alcohols and polyalkylene derivatives of hexitol anhydride fatty acid esters, and an inert conditioning agent, the proportions of soap, surface-active agent and conditioning agent being about 0.05-2.0%, 0.025-0.75% and 0.25-5.0%, respectively of the weight of the salt.

3. A free-flowing, non-caking salt composition consisting essentially of sodium chloride having a water repellent metal soap adhering to the particles thereof, and a surface-active agent of the group consisting of sulphonated amides, substituted ammonium compounds, cyclic quaternary ammonium compounds, polyethylene glycol fatty acid esters, alkyl aryl polyether alcohols and polyalkylene derivatives of hexitol anhydride fatty acid esters, the proportions of soap and surface-active agent being about 0.05-2.0% and 0.025-0.75%, respectively, of the weight of sodium chloride.

4. A free-flowing, non-caking salt composition consisting essentially of sodium chloride having a water-repellent metal soap adhering to the particles thereof, a surface-active agent of the group consisting of sulphonated amides, substituted ammonium compounds, cyclic quaternary ammonium compounds, polyethylene glycol fatty acid esters, alkyl aryl polyether alcohols and polyalkylene derivatives of hexitol anhydride fatty acid esters, and an inert conditioning agent, the proportions of soap, surface-active agent and conditioning agent being about 0.05-2.0%, 0.025-0.75% and 0.25-5.0%, respectively, of the weight of sodium chloride.

5. A free-flowing, non-caking salt composition as defined in claim 3, wherein the surface-active agent consists of a sulphonated amide in an amount not exceeding about 0.50% of the weight of sodium chloride.

6. A free-flowing, non-caking salt composition as defined in claim 3, wherein the surface-active agent consists of a cyclic quaternary ammonium compound in an amount not exceeding about 0.20% of the weight of sodium chloride.

7. A free-flowing, non-caking salt composition as defined in claim 3, wherein the surface-active agent consists of a polyalkylene derivative of a hexitol anhydride fatty acid ester in an amount not exceeding about 0.20% of the weight of sodium chloride.

8. A free-flowing, non-caking salt composition as defined in claim 4, wherein the surface-active agent consists of a sulphonated amide in an amount not exceeding about 0.50% of the weight of sodium chloride.

9. A free-flowing, non-caking salt composition as defined in claim 4, wherein the surface-active agent consists of a cyclic quaternary ammonium compound in an amount not exceeding about 0.20% of the weight of sodium chloride.

10. A free-flowing, non-caking salt composition as defined in claim 4, wherein the surface-active agent consists of a polyalkylene derivative of a hexitol anhydride fatty acid ester in an amount not exceeding about 0.20% of the weight of sodium chloride.

11. A free-flowing, non-caking salt composition consisting essentially of sodium chloride having a water-repellent alkaline-earth metal soap

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adhering to the particles thereof, and a surface-active agent consisting of a polyalkylene derivative of a hexitol anhydride fatty acid ester, the proportions of soap and surface-active agent being about 0.05-2.0% and 0.025-0.20%, respectively, of the weight of sodium chloride. 5

12. A free-flowing, non-caking salt composition consisting essentially of sodium chloride having a water-repellent alkaline-earth metal soap adhering to the particles thereof, a surface-active agent consisting of a polyalkylene derivative of a hexitol anhydride fatty acid ester, and an inert conditioning agent, the proportions of soap, surface-active agent and conditioning agent being about 0.05-2.0%, 0.025-0.20% and 0.25-5.0%, respectively, of the weight of sodium chloride. 10 15

13. A free-flowing, non-caking salt composition consisting essentially of sodium chloride having magnesium stearate adhering to the particles thereof, polyoxyethylene sorbitan monolaurate, and magnesium carbonate, the propor- 20

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tions of magnesium stearate, polyoxyethylene sorbitan monolaurate and magnesium carbonate being about 0.20-0.30%, 0.10-0.20% and 2.0-3.0%, respectively, of the weight of sodium chloride.

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Certificate of Correction

Patent No. 2,539,012

January 23, 1951

HORACE W. DIAMOND ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 1, line 6, for "practially" read *practically*; column 3, line 4, for the words "as much" read *a much*; column 4, line 64, for "4.5%" read *4-5%*; column 5, line 22, for "Hytergren" read *Hytergen*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 20th day of March, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

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