SOME EXPERIENCES IN PREPARING EMULSION OF SILVER IODIDE.*

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The so-called emulsion of silver iodide is a suspension of this compound in some suitable vehicle. It is probably well known to some and a total stranger to many others.

This subject has been treated by Mr. M. I. Wilbert in the *American Journal of Pharmacy* for February, 1906, and by Mr. J. K. Thum in the same journal for November, 1910, and November, 1915. Mr. Wilbert, where cited, mentions the availability of Irish moss, quince seed, salep and tragacanth as suspending media, and suggests a type-formula in which the silver iodide is first produced and then suspended in mucilage of Irish moss. Mr. Thum used the yolk of fresh eggs with ideal results, but brought about the formation of silver iodide in the presence of the yolk, instead of first forming the silver iodide and then suspending it as suggested in Mr. Wilbert's formula. Mr. Thum described mucilage of Irish moss as being, next to the egg yolk, the most efficient and satisfactory agent. Mr. Thum also used solutions of gelatin ranging in strength from 0.1 to 0.5 percent, which after frequent shaking during twenty-four to thirty-six hours brought the silver iodide into suspension; the solution containing 0.3 percent gelatin is mentioned as giving almost perfect results.

But it was our good fortune to be ignorant of this specific information, when about two years ago a physician gave an order for some five percent silver iodide emulsion to be ready in half an hour. We knew how to make silver iodide, but we had never been called upon to suspend it, and our inexperience in the matter gave us no little concern as we reflected on the possibility of turning out a satisfactory product..

We knew that an " emulsion " of silver iodide is used for photographic plates, and that gelatin is employed in this connection as the emulsifying agent, but not in a manner fit for our needs. Running over the list of eligibles in our minds, we felt that any one of several mucilages recalled might be as well suited as gelatin, and someone among us in the store remembered having heard of mucilage of Irish moss being used for the purpose. Coincidentally we were thinning some mucilage of tragacanth for pasting labels, and grasping the opportunity we took advantage of its readiness, and in less than the allotted time had an emulsion of fine appearance in the physician's hands. He remarked that he would need more within a few days, so we immediately prepared another portion with the mucilage of tragacanth, both to be ready and also to learn how well it would keep. For comparison, another lot was made with the aid of mucilage of Irish moss. Within a few days the emulsion produced with tragacanth had begun to darken somewhat and showed a tendency to settle a coarse curdy precipitate, while that made with Irish moss retained its light yellow color and consistence for a much longer time. In fact, the color never perceptibly changed, although the silver iodide settled to some extent in the bottle.

Later, the physician reported that the lot which he received had retained its original appearance until used. But the use of Irish moss mucilage had, to our minds, improved the appearance and stability of the product so greatly that we decided to use it until an opportunity to look further into the matter of suitable suspending agents should come.

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Accordingly, we examined mucilages made from sassafras pith, flaxseed, salep, elm, quince, dextrin, starch, and acacia, all of which are well known in use as emulsifying agents and emollient vehicles. We also repeated our experiments with tragacanth and Irish moss, and at the same time tried solutions of gelatin and egg albumen. Yolk of egg was not tried during this period, for it was looked upon as of itself too readily changeable.

After our experiments had been made and our conclusions drawn, we were apprised of the articles written by Mr. Wilbert and Mr. Thum. We have said it was our good fortune to be ignorant of the specific information given by these gentlemen; now the reason for so saying is not that we do not appreciate their work nor declare for their priority on all points in common, but had we known of their publications we most likely would not have made the many experiments performed for the purpose of this paper, and thereby would have been deprived of such knowledge as we have gained through personal experience with this subject. However, we present our experiences because they not only essentially conform to and thus confirm the statements of these gentlemen, but also mention some matters of interest not touched upon in their contributions.

Our object in making these experiments was to devise a plan to quickly produce a finely divided suspension of silver iodide and do so by introducing as little suspending material as possible.

Silver iodide is affected by light, especially the actinic rays, when concentrated by a lens, but it is not so rapidly affected by diffused daylight or artificial light that it shows perceptible change in the time required to make an emulsion, and for that reason none of these processes need to be conducted in a dark room. Indeed, silver iodide has proven to be so permanent in these emulsions that we look upon the theory of its use as an antiseptic as somewhat of a conjecture of fact and fancy, to be settled by each practitioner for himself.

Unless otherwise specified our experiments were made on the basis of five percent silver iodide. Where a recognized formula for a mucilage existed, the prescribed strength and mode of preparation was followed, and the product used in the first trials with each individual mucilage.

The amounts of silver nitrate and potassium iodide needed to give the required quantity of silver iodide were calculated from the terms of the following well-known reaction:

$$\underset{168.69}{AgNO_3} + \underset{164.76}{KI} = \underset{233.02}{AgI} + \underset{100.43}{KNO_3}$$

the symbols of which, designated in molecular weights, as shown under them, respectively, indicate that 168.69 parts of silver nitrate require 164.76 parts of potassium iodide to produce 233.02 parts of silver iodide with the simultaneous formation of 100.43 parts of potassium nitrate.

In the course of this paper it will be pointed out that the specific gravity of mucilage of Irish moss, no matter how long macerated when prepared, is but negligibly more than water, therefore in our calculations for a five percent suspension we used 456 grains, or the weight of a fluidounce of water, as the 95 percent of vehicle per fluidounce, which calls for twenty-four grains of silver iodide as the five percent sought. By ratio, we find that 17.375 grains of silver nitrate is required to yield this silver iodide. A close scrutiny of the figures involved in the chemical reaction reveals the fact that just a little more of silver nitrate is required than of potassium iodide for accurate and complete interchange with each other.

Now the United States Pharmacopœia requires silver nitrate to be practically pure, so no allowance need be made on its part for impurities. But the same authority permits potassium iodide to contain one percent of impurities, consisting chiefly of chloride, carbonate and free hydrate, hence some allowance must be made for their most probable presence; and to commensurate for any deficiency of actual iodide, it has been suggested to use a slight increase over the theoretical amount of potassium iodide, and make the quantities of the two chemicals equal. This was invariably done by us, after we had learned by experience that as little as one-fortieth of a grain of unaffected silver nitrate which might remain in solution would very rapidly bring about discoloration of Irish moss mucilage.

There can be but little, if any, objection found to the presence of a minute excess of potassium iodide over that actually required, as it is imperative to completely precipitate the silver so that no soluble salt of it remains in solution, to act either as an undesirable application or as a factor to discolor the emulsion.

For quantities greater than one ounce of five percent emulsion, simply multiply 17.375 grains by the number of ounces required.

Silver iodide can, of course, be precipitated, washed, and then suspended in a mucilage, although it requires longer time to get it finely divided by agitation or stirring, and for this reason the plan is not so well suited for hurried calls.

The products of our numerous attempts with this plan were not nearly so uniformly satisfactory as when the silver and potassium salts were dissolved each in one or two fluidrachms of distilled water and each solution diluted with a mucilage to half an ounce before mixing to form the insoluble silver iodide. In other words, the smoothness of the suspension was almost always superior when the reaction was brought about in the presence of a suitable mucilage, and if there is any chemical activity in the preparation, or if it is used solely as a protective application, it must be granted that the more finely divided the silver iodide the greater its efficiency.

When the precipitated silver iodide is not washed before suspending it, the emulsion will, of course, contain the potassium nitrate produced in the reaction, as also any excess of potassium iodide and other soluble salts originally present in the potassium iodide.

The amount of potassium nitrate formed in the preparation of a five percent emulsion is 10.34 grains per fluidounce, which equals a 2.27 percentage strength, which is three to four times the strength of the usual physiological or normal salt solutions. When intended for use in the eye, it may be thought necessary to rid the emulsion of soluble salts, although this may not be necessary in all cases, especially when we recall that ten to fifteen grains of borax or other salts are not infrequent ingredients in a fluidounce of eye drops. As a genito-urinary application the presence of these potassium salts is probably of little moment.

But if, for any reason, the emulsion must be free from soluble salts, the silver iodide may be produced from the water solutions of the necessary substances, thoroughly washed with either hot or cold water by decantation, and then incorporated in the suspending medium. Mucilage of Irish moss will serve here either hot or cold. Experience demonstrates that silver iodide settles very rapidly in hot water, and the expectation here would be to see the same thing happen; on the contrary, however, the hot mucilage envelops the silver iodide and overcomes this tendency to settle. Or, as we have found to be thoroughly practical when mucilage of Irish moss was employed, the emulsion may first be prepared by precipitating the silver iodide in the presence of the mucilage and the product then subjected to dialysis, using the ordinary parchment powder papers of the store as the necessary septum.

The former plan, for some reason which we have been unable to discern, unless it be attributed to allotropic conditions of the silver iodide, does not always show as smooth suspensions as would be desired; while the process of dialysis has almost always shown an improvement in this appearance, and has proven a simple expedient in ridding the emulsion of all crystalline matter.

Should it be deemed necessary to sterilize the emulsion either with the salts present or removed, it will be found that the preparation made with Irish moss will withstand this process. A sample subjected to streaming steam for three successive periods of twenty minutes each showed no change except a tendency to thicken slightly on the top surface, and was readily restored by shaking.

When silver nitrate was added to the several mucilages examined some of them showed a tendency to gelatinize, but none of them showed any appreciable precipitate of chlorides, so none were disqualified for such a cause.

Mucilage of sassafras pith, U. S. P., two percent, failed to suspend the silver iodide, as did also a ten percent strength of mucilage. Both products showed stringy coagulations and curds and upon standing and shaking did not improve in miscibility.

Mucilage of flaxseed, twenty percent, did not serve the purpose nor did one of 100 percent strength. The silver iodide went down in veritable lumps which were difficult and sometimes impossible to shake through the liquid.

Mucilage of salep, N. F., one percent, did not satisfactorily suspend either three or five percent of silver iodide, and failed to preserve it; while a five percent salep mucilage suspended three percent of silver iodide moderately well, but very soon showed a change in color.

Mucilage of elm, U. S. P., six per cent, was not a satisfactory suspending medium by any means; neither was a twenty percent strength. This mucilage behaved very much like mucilage of sassafras pith.

Mucilage of quince, N. F., Appendix, of two percent strength and even one of double strength did not suspend either three or five percent of silver iodide. The ten percent mucilage yielded variable results, since in some instances it failed outright and discolored, while in others it gave quite satisfactory effects; and one of the most presentable three percent emulsions, obtained from any experiment we made, was afforded by a twenty percent mucilage of quince after twelve hours, almost without shaking, although when first made it was a hopeless looking mess of feathery precipitate. We have never been able to exactly duplicate this particular result, which emphasizes the uncertainty of quince mucilage. In the weaker strengths, when the mixtures did not approximate suspension, discoloration was soon observed. When silver nitrate is added to quince mucilage it coagulates it to an almost jelly consistence which requires long stirring to render it sufficiently thin to enable one to proceed with the work. It will therefore be recognized that quince mucilage is very poorly adapted to the purpose.

Mucilage of dextrin, N. F., thirty-three and one-half percent, suspended the silver iodide, but decomposition began to show almost immediately.

Mucilage of starch, B. P., was prepared by thoroughly cooking starch with boiling water in the proportion of twelve grains to the fluidounce. In this strength of starch mucilage the silver iodide mixed, but quickly settled, leaving a perfectly clear supernatant liquid of about one-third to one-half of the volume. This preparation had the distinction of being the only one from which the emulsified part separated to leave a clear liquid. A mucilage of twenty-four grains to the fluidounce behaved similarly.

Starch showed but very little tendency to discolor, and seems to be suitable so

far as appearance of emulsion is concerned, although on several occasions samples of it became mouldy and displayed a musty odor within a week.

Mucilage of acacia, made according to the U. S. P. formula of thirty-four percent with thirty-three percent of lime water, had a slight acid or nearly neutral reaction. An alkaline mucilage must, of course, be avoided. The slightly acid mucilage of acacia gave good results, as did also a mucilage of the same strength made without lime water and possessing a strong acid reaction to litmus.

Half strength and quarter strength mucilage of acacia also showed good effects. These mucilages contain so much more solids than Irish moss mucilage, however, that they cannot be recommended in its stead.

Mucilage of tragacanth, U.S.P., six percent, made with or without glycerin, was entirely too viscid, but reduced to one-quarter strength with water it suspended the silver iodide quite satisfactorily, but upon standing for a week or more showed in some samples an inclination to granulate, although some products containing it stood for months without showing much change in color. It can well be considered fit for any emulsions intended for prompt use; although it cannot be prepared as quickly as mucilage of Irish moss and for this reason is not as desirable.

Solutions of gelatin were tested as emulsifying agents only to find that concentrated ones were impractical to use in the presence of silver nitrate because it coagulated the gelatin so intensely; and that solutions which are diluted sufficiently to permit the addition of silver nitrate have very little immediate suspending action on it. For these reasons gelatin was discarded.

Egg albumen in full strength was coagulated so firmly by silver nitrate that it was rejected. Diluted with an equal volume of water it could be put through the process, but the result was a very curdy precipitate and so far from being satisfactory as scarcely to deserve mention along with Irish moss, tragacanth, acacia and starch.

In our original experiments little attention was intended to be given suspending media of animal origin, for the reason that they would putrefy. But after reading Mr. Thum's notes on this subject we decided to repeat our tests with gelatin and egg albumen, and also try yolk of egg. As reported by Mr. Thum, we also found yolk of egg to be a very efficient and prompt suspending material, but the emulsion began to show a change in color in less than a week.

Compared with the preparation from Irish moss, it cannot be considered in any way superior.

From the foregoing statements it will be observed that some of the mucilages which have been treated of satisfactorily suspend silver iodide but discolor so rapidly as to be impractical, while others among them did not suspend it at all, even when tried in much greater strength than the recognized formula for that particular mucilage.

We have now reached mucilage of Irish moss, N. F., three percent. It is undoubtedly the best practical emulsifying agent of all examined for the purpose, as every trial and test of it has proven. Its dependability and stability will unquestionably gain for it the commendation of all who try it for this purpose.

But before proceeding to tell the results of the experiments with the mucilage and silver iodide, mention should be made of some of the properties of Irish moss itself which were observed during these experiments. When dried it loses but a trifle in weight, indicating an almost total absence of moisture in its make-up.

The sample we examined and used for these experiments showed a loss of approximately ten percent of weight through the washing required to remove all but a faint trace of chlorine; the chlorine so removed represented in terms of

sodium chloride six percent of the original substance. The water-insoluble substances present in the sample of moss amounted to ten percent, which indicated a total of eighty percent of available water-soluble matter for mucilage.

As hereinbefore stated, it is a remarkable fact that a fluidounce of mucilage of Irish moss made according to the N. F. directions weighs but two and a half to three grains more than a fluidounce of water, making the increase in specific gravity over water practically negligible in all calculations, as it affects but the third decimal place. This fact remains the same whether the mucilage is prepared with hot or cold water. A fluidounce of the mucilage was evaporated in a platinum crucible in order to check up this paradox; the residue weighed less than three grains.

Mucilage of Irish moss is practically neutral to litmus paper, for it shows but the faintest acidity, and a very minute amount of fixed alkali will render several ounces of the mucilage alkaline to litmus and phenolphthalein.

Mucilage prepared by macerating Irish moss in cold water serves in every respect as well as the mucilage prepared with hot water and allowed to cool.

A series of mucilages were made by maceration in cold water for periods of fifteen minutes, thirty minutes, one hour and three hours, respectively, with the result that a fluidounce of the thirty minutes, one hour and three hour samples were on an average within a grain of each other in weight, while the fifteen minute sample was within half a grain of the weight of the thirty minute specimen, demonstrating that thirty minutes maceration with cold water will produce a satisfactory mucilage.

After a number of tests made with the mucilage prepared in strict accordance with the N. F. directions, we finally devised the following plan, basing it on the results of our experiments:

Rejecting brown and harsher portions of the moss, select a few well-bleached and finely curled pieces to obtain the weight required; place these in a graduate and wash with several changes of water; as the texture softens, spread the branches to insure thorough washing; six to eight changes of water within two to three minutes will be found to be sufficient to remove the adhering chlorides. By this time the moss begins to swell and display a gelatinous surface and a test of the washings made now will show but a faint indication of chlorides. There need be no fear of overdoing the washing and thus losing mucilage, for as has been pointed out there will be an abundance of mucilage left to saturate the water. The moss is now macerated in a fresh portion of cold water with frequent stirring for half an hour, then expressed through well-washed muslin used double thick to obtain a clean mucilage. For each fluidounce of five percent emulsion to be made, 17.375 grains of silver nitrate are to be dissolved in one fluidrachm of water and this solution mixed with three fluidrachms of mucilage of Irish moss. The same amount of potassium iodide should be dissolved in one fluidrachm of water, and its solution diluted to four fluidrachms with mucilage. The two solutions are now to be mixed by stirring together in order to thoroughly break up any curds of the silver iodide and facilitate suspension. The product may now be transferred to suitable containers.

In carrying out this process, it will be noted that the addition of silver nitrate to mucilage of Irish moss shows but little opalescence; but the silver nitrate causes the mucilage to thicken almost to the point of gelatinization, although it can be stirred into a uniform consistence. On the other hand, the effect of the potassium iodide was to lessen the viscidity of the mucilage of Irish moss.

The entire quantities of the solutions may be mixed at once, or one may be gradually poured or dropped into the other with constant stirring; there appears

to be but little difference in behavior, unless it be that, when the entireties are mixed, more time is required to shake or stir into a uniformity of appearance. It seems not to matter which solution is poured into the other, for although silver iodide will dissolve in concentrated solutions of potassium iodide, the solution here employed is entirely too weak even in the beginning and of course is becoming weaker and weaker as the reaction progresses. The emulsions prepared with mucilage of Irish moss present at the time of reaction have seldom, if ever, failed to be smooth and uniform. We have never had a sample prepared in this manner darken or display any decided change in color, but we have had several samples made by first precipitating the silver iodide, washing, and then suspending, begin to darken within a few days.

Emulsions made with Irish moss may be diluted with water or with moss mucilage to make weaker preparations. Dilutions made with water settle more rapidly than those made with mucilage—a natural inference. Suspensions in Irish moss never settled entirely clear, as did starch emulsions. When the precipitate does settle in moss mucilage it appears to be still enveloped by the viscidity of the vehicle and may be easily restored by shaking. A sample prepared last August demonstrates this condition very effectively. It is also possible to make a ten percent emulsion with moss mucilage, a sample of which prepared a few months ago is here shown (at Association meeting).

Owing to the heavy nature of silver iodide, it is evident that no emulsion should be used without shaking. In all of our experiments flint glass vessels and containers were used, and found to be thoroughly practical, and prolonged contact with cork stoppers has not in the least affected any of the emulsions which were satisfactory when first made, circumstances which compel us to believe that when once formed and protected with mucilage, silver iodide is quite a stable substance; in fact a sample exposed to bright direct sunlight for two days darkened but little, while a specimen unmixed with mucilage of Irish moss had turned dark gray within an hour under the same influence.

Failing in an attempt to filter an emulsion made with Irish moss, it occurred to us to dialyze it as a means of removing the salts in solution, and as a septum we used ordinary parchment powder papers. It required about twenty-four hours and five or six changes of water to extract practically all of the soluble salts. The emulsion was improved in appearance and consistence, through the removal of the crystalline constituents. A comparison was made by allowing a few drops of the original emulsion to spontaneously evaporate upon a smooth glass surface, with the result that the salts in solution were left as a crystalline centre in the residue, while a like performance with an emulsion from which the salts had been dialyzed showed no such crystalline residue, but instead a surface and appearance almost as smooth as a photographic plate.

The potassium nitrate left in the emulsion prevents the mucilage from decomposing, at least so far as odor is evidence. A sample prepared in August, 1915, gives no indication through odor of any change, whereas mucilage of Irish moss alone will within a week to ten days become obnoxious. Likewise, an emulsion from which the salts had been dialyzed developed an odor of putrefaction within a couple of weeks.

While it is evident that emulsion of silver iodide prepared by the method outlined will keep indefinitely, still if there is but an occasional call for it, and no need of keeping it ready made, the plans here and elsewhere given furnish a quick and thoroughly practical method for its production. But no matter which vehicle is used the facility with which silver salts are reduced by certain agents

must be remembered so that all utensils used will be scrupulously free from such disturbing causes, for aside from these there is little chance of failure.

Upon comparing mucilage of Irish moss with the other available vehicles, its advantage over tragacanth will be seen to lie in the ease of preparation; while its preference over starch and acacia comes through it introducing so little substance into the preparation.

The advantages of mucilage of Irish moss may then be emphasized as follows:

It can be depended upon as an efficient suspending agent.

It is easily and quickly prepared.

It gives a permanent emulsion.

It supplies a sufficiently viscid medium though adding but a trifle of solid matter.

It is as inert as any other suitable substance.

It is inexpensive.

While yet concerned with this subject a few words will be said regarding the sulphur which is present in Irish moss. To one who had never incinerated a vegetable drug and found a mass of hepar sulfuris as the resulting ash, it was a revelation to encounter such when some unwashed Irish moss was subjected to a bright red heat. With a lower heat very little sulphide is formed, but raised to bright redness, one can see a phosphorescence as of free sulphur burning, although sulphur dioxide could not be detected by odor. The fused mass amounted to 21.25 percent of the original weight. Chlorides were present, of course.

Sulphates, earthy phosphates, carbonates, iron, aluminum, and silica were other constituents encountered in the examination of this ash, but no complete analysis was attempted.

A second weighed portion of moss was washed until it began to gelatinize, then dried and ignited. The result showed ten percent of ash and contained abundant alkaline sulphides, and a little chlorides.

A third weighed portion was completely exhausted by repeated applications of boiling water, the residue was dried and weighed. This insoluble part represented ten percent of the original substance. It was next incinerated and found to yield 2.5 percent of ash, calculated on original moss. The ash from this treatment was snow-white; it contained neither chlorides nor sulphides, but consisted of silicious matter. It is worthy of remark that in whatever form the sulphur exists in Irish moss, it has arranged itself in a very accommodating manner, so far as our present use for the mucilage is concerned.

SYRUP OF TEA FOR ICED TEA.*

BY CHARLES H. LAWALL AND M. R. LAWALL.

One of the overlooked opportunities of the pharmacist during the summer season is the preparation and sale of a concentrated syrup from which iced tea may be instantaneously made by the simple addition of water, ice and lemon.

Iced tea is one of the most popular of summer drinks taken with meals either at home or in restaurants. It is somewhat of a bother to prepare in the home and the average housekeeper would doubtless welcome a simplification of this portion of her summer work connected with the family menu.

That the plan is practicable and the syrup permanent when properly made has

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