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METHOD OF TESTING NICOTINE SOLUTIONS.

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This invention relates to an improved method of testing nicotine solutions.

The object of the invention is to provide a process which can be carried out quickly and with much less apparatus than has heretofore been employed.

Nicotine solutions are now widely used in large baths for dipping cattle, sheep and other domestic animals for the purpose of freeing them from various kinds of insects, such as ticks, lice, etc. The nicotine content of these baths must be kept within certain limits. If too weak it will not kill all the insects; if too strong it will injure or kill the domestic animals, and, in any case, if more nicotine be used than is necessary to kill all the insects, the expense of dipping is materially increased on account of the cost of the unnecessary nicotine in the bath. For these reasons, the strength of a nicotine dipping bath is prescribed by the United States Department of Agriculture and by State regulations. To fulfill these requirements it is necessary to make frequent tests at the places where the baths are being used. Moreover, these tests must be made in most cases by men who are not trained chemists.

Experience has shown that methods of test heretofore employed have necessitated a collection of apparatus and chemicals which not only required careful packing, but in spite of such care, was frequently injured in shipment. Such a collection of apparatus and chemicals, heretofore, has included 16 pieces of equipment besides a specially built box or carrying case fitted with compartments, and slips and springs for properly holding the glassware and chemicals. By the present invention, this field test kit is greatly simplified, so that only seven pieces of equipment (aside from the box or other container) are needed, and are of such nature that they may be readily and safely packed in a plain box much smaller than the carrying case heretofore employed.

The determination of nicotine in a dipping bath is complicated by the fact that such baths contain much extraneous matter, particularly organic compounds of a nitrogenous character which would combine with the usual reagent (silico-tungstic acid) employed for determining the amount of nicotine in the bath sample. Hence, it has been customary heretofore to precipitate these impurities, and then filter the sample, the filtrate, only, being treated with the silico-tungstic acid, the filtration step being necessary because the precipitates heretofore produced would react with the silico-tungstic acid and thereby materially affect the resultant determination of nicotine.

I have discovered that silico-tungstic acid may be protected against the reactive effects of the organic impurities by tungsten trioxide (WO_3) without necessitating the removal by filtration of the precipitates which may be formed by the interaction of such organic impurities and the tungsten trioxide, if the sample of bath tested be slightly acid or be acidified in the proper manner. I have found, further, that a solid acid capable of forming complex acids with inorganic metal acids, and particularly oxalic acid, is especially suitable for the acidification of the bath sample where tungsten trioxide is used. Oxalic acid in solid form has the further advantage that it may be mixed with the tungsten trioxide without interfering with the results, thus permitting the mixture to be put up in predetermined charges suitable for field testing purposes, as will be clear from the description hereinafter.

The invention will now be described more specifically, commencing with a specific description of a field kit suitable for carrying out the test.

In carrying out the process in the field, a so-called field kit is employed. In one specific form this comprises the following:

(1) An eight ounce bottle containing an aqueous solution of silico-tungstic acid, preferably of a certain special strength as hereinafter more fully explained, and which will be designated as the test solution.

(2) A suitable number (generally 12) of gelatine capsules, each containing a mixture of powdered oxalic acid and powdered tungsten trioxide, or tungstic anhydride, (WO_3), the total amount of the mixture in each capsule being about 3.75 gms., of which the oxalic acid amounts to 1.25 gms. and the tungstic acid to 2.5 gms.

(3) A box of filter paper.

(4) A 50 c. c. column or cylinder gradu-

ated in cubic centimeters, the diameter of the column preferably being such that the graduations will be about 2.5 mm. apart. A column having an interior diameter of about 22 mm. will give this result. The graduations are also numbered at every fifth mark from the top downward, the uppermost mark being zero. The numberings are decimal fractions as .01; .02; .03; etc., and are intended to indicate percentages of nicotine, as will be clear from the description hereinafter. In practice, there may be intermediate marks half-way between the others and numbered .015; .025; .035; etc., but this is not important.

(5) An ordinary 8 oz. bottle which will be referred to hereinafter as the "shaking" bottle.

(6) An ordinary dropper comprising a glass tube with rubber bulb.

(7) A black slab having at least one, and preferably two, slight concavities in the top, these being of such size that each will hold slightly more than 6 drops of liquid, that is, about 388 milligrams. This will be referred to hereinafter as the test slab.

With this field kit, the test is carried out as follows:

From a sample of the bath liquor to be tested there is poured enough to fill the graduated column to the uppermost mark, viz, the 50 c. c. mark. This bath liquor is poured from the column into the shaking bottle. Then the contents of one capsule is dumped into the shaking bottle. A foam may form in the bottle. As soon as this is gone, the contents of another capsule is dumped into the bottle. After any foam which is caused by this has disappeared, the bottle is well corked and well shaken for not less than half a minute, and allowed to stand.

The graduated column is now washed in clean water and then rinsed with a small amount, say 5 c. c. of test solution, the rinse liquor being thrown away. Then this column is filled with the test solution to its uppermost mark (50 c. c.).

It is now necessary to pour some of the test solution from the graduated column into the shaking bottle. As it is important not to add any more than is necessary to combine with all the nicotine in the liquor in the shaking bottle, certain precautions are necessary to avoid supplying too much. Hence, the first effort is to supply somewhat less than enough test solution. In general practice it has been found that about 20 c. c. of test liquor may be added at once. To do this, the test solution is poured from the graduated column until the amount left therein is level with the graduation numbered .04. This means that experience has shown that the dipping bath under test usually contains more than .04% nicotine. The shaking bottle is again corked and well shaken for at least thirty seconds or even longer.

One of the filter papers is now folded into a quadrant and opened to form a cone, being held between the thumb and forefinger by the side with three thicknesses of paper, thus forming a conical filter. This filter is then filled about half full of liquid from the shaking bottle. The first ten drops of the filtrate are allowed to drop back into the shaking bottle, and then five drops are allowed to drop into each of the concavities in the test slab. The filtered liquid in these concavities is examined to make sure it is perfectly clear. If it is not, this indicates that the filtration through one piece of filter paper is not sufficient, which sometimes occurs with some dipping baths. In this case, the test slab must be well-washed, and the filtration procedure repeated using two or more sheets of filter paper.

When a clear filtrate is obtained in the concavities of the test slab, the procedure is as follows:

The dropper is charged with test solution from the bottle containing it and then a single drop of such solution is added to one, only, of the two test samples of filtered fluid in the concavities in the test slab. This ought to cause a whitish cloud of precipitate to form, which will be clearly seen in a good light. The presence of the precipitate is also more readily recognized by comparison with the adjacent untreated test sample in the other concavity of the test slab. If no cloud or precipitate is formed, this proves that too much test solution was poured into the shaking bottle. Under this condition the entire test must be repeated from the beginning commencing with another 50 c. c. of bath liquor and proceeding as hereinbefore described but using a lesser quantity of test solution in the shaking bottle.

If a cloud or precipitate is formed in the treated test sample in the slab, then more test solution should be poured from the graduated column into the shaking bottle, the test slab should be thoroughly cleaned, and a further test of a filtered sample of 5 drops should be made as before. If this shows a cloud of precipitate, another portion of test solution should be added to the shaking bottle and a further filtered sample tested in the slab. In making the addition or additions of test solution to the shaking bottle, only a small quantity should be added each time, for example, say, first 20 c. c. and then 2½ c. c. each time, or, reading by the numbers on the graduate, first, until the remaining liquid in the graduate stands at the number .06, and, second, where it would show .06½. If there is a third addition or more, these additions would be about 2½ c. c. each.

So soon as a test sample in the test slab fails to show a cloud, the test is completed. The percentage of nicotine in the dipping bath is at once read off from the graduated column, at the level of the portion of test solution remaining therein.

In order that this test can be carried out with sufficient accuracy to suit the requirements by persons not skilled chemists, it is important to use such a dilute test solution that a quantity readily noticeable by untrained users may be poured from a graduated column, such as described, into the shaking bottle and yet carry in a very small amount of silico-tungstic acid. This also reduces the error due to any errors in reading the level of the test solution in the graduate. Furthermore, by preparing the test solution of the proper strength, it is possible to mark the numbers indicating percentage of nicotine in even hundredths opposite the usual graduations on the graduated column. Instead of etching in these numbers, or figures, they may be marked on a strip of paper or the like and the latter pasted or cemented to the graduate and varnished. With such a strength of silico-tungstic acid solution and such a graduated column, it is possible to reduce the amount of equipment in the field kit, which heretofore required a glass graduate to measure the 50 c. c. sample of the bath liquor, and a glass burette with which to titrate the treated bath liquid. Thus in place of two pieces of glassware, one of which, the burette, was relatively expensive, easily broken and difficult to pack properly, I substitute one piece, viz, the graduated column of such a size and shape that it is not fragile or difficult to pack, and which will give a convenient reading of the nicotine percentages.

In order to accomplish these results, the test solution should have such a percentage strength of silico-tungstic acid that the amount of the latter in one c. c. of water would be an equivalent for one milligram of nicotine. Theoretically this would be about 0.877 gms. $SiO_2 12WO_3$ per 100 c. c. of water, but in practice it has been found that silico-tungstic acid, as obtained on the market, varies so much in its quantitative reaction with nicotine, that it is generally necessary to prepare the solution of a strength certainly above that desired, test it with a nicotine solution of known strength to determine its equivalence, and then dilute it down to the strength designated above.

By the use of tungsten trioxide and a solid acid such as oxalic acid, the field kit is considerably simplified and danger of injury to it in transportation is avoided, because the bottle of liquid acid, usually hydrochloric acid, heretofore employed, is dispensed with. Experience has shown that with such liquid acid the cork of the bottle often was worked loose during transportation and the acid escaped and ruined the kit.

The use of tungsten trioxide makes it possible to pour the test solution directly into the sample of the bath in the shaking bottle, thereby avoiding the step of filtration which has heretofore been necessary. Hence, the glass filter funnel, which has been necessary in the prior field test kits, may be omitted, and the amount of filter paper to be packed in the kit is reduced one-half. This results from the fact that tungsten trioxide in an acid solution will protect the silico-tungstic acid against the reactions of organic impurities in the bath sample, and can be used in some excess without affecting materially the quantitative reaction between the nicotine and the silico-tungstic acid. Hence, it is possible to put up a predetermined charge of tungsten trioxide large enough to take care of all the impurities found in a 50 c. c. sample of the foulest dipping bath encountered in practice, but which will not interfere with the reaction of nicotine and silico-tungstic acid when used with a relatively clean dipping bath.

The oxalic acid, also may be put up in a predetermined charge for a 50 c. c. bath sample, without any danger of failing to acidify the bath sufficiently or of over acidifying it, probably because little or none of it combines with anything likely to be found in a dipping bath, or, at least, not in such a way as to affect the test. This avoids the necessity of indicators, such as Kongo paper, which have heretofore been necessary in acidifying bath samples with liquid acids, such as hydrochloric acid, and also avoids the steps necessary in using such indicators.

It may be that the reason why any excess of oxalic acid and tungsten trioxide do not affect the quantitative reaction of the nicotine and silico-tungstic acid is because any such excess of either enters into combination with the other to form a complex compound. Whether this be the true explanation or not, it has been found by experience that there is a considerable latitude in the quantities of oxalic acid and tungsten trioxide used with 50 c. c. samples of baths which vary greatly in the amounts of organic impurities. For example, the amount of oxalic acid for such a sample may vary from 2 to 3 gms., and the tungsten trioxide from 3 to 10 gms. without seriously affecting the accuracy of the test. However, it is better to prepare the capsule charges in the proportions hereinbefore specified, and then the user, if encountering a specially foul bath may add the contents of three or four capsules, instead of only two, to the 50 c. c. sample.

What is claimed is:

1. The process of determining the nicotine content of a solution containing nicotine and organic impurities such as occur in dipping

baths, which consists in acidifying the solution, adding tungsten trioxide in amount not less than sufficient to combine with all the said organic impurities and then directly titrating the said solution with silico-tungstic acid.

2. The process of determining the nicotine content of a solution containing nicotine and organic impurities such as occur in dipping baths, which comprises adding a solid acid capable of forming complex acids with inorganic metal acids to the solution to acidify it slightly, also adding tungsten trioxide in amount not less than sufficient to combine with all the said organic impurities and then directly titrating the said solution with silico-tungstic acid.

3. The process of determining the nicotine content of a solution containing nicotine and organic impurities such as occur in dipping baths, which comprises adding oxalic acid in solid form to the solution to acidify it slightly, also adding tungsten trioxide in amount not less than sufficient to combine with all the said organic impurities and then directly titrating the said solution with silico-tungstic acid.

4. The process of determining the nicotine content of a solution containing nicotine and organic impurities such as occur in dipping baths, which consists in adding a mixture of tungsten trioxide and oxalic acid, as solids, to the solution and then directly titrating the resultant solution with silico-tungstic acid.

5. The process of determining the nicotine content of a dipping bath, which consists in adding oxalic acid and tungsten trioxide to a sample of such bath, in the proportions of 2 to 3 gms. of oxalic acid and 3 to 10 gms. of the tungsten trioxide to 50 c. c. of the bath sample, and then directly titrating the resultant solution with a silico-tungstic acid solution.

6. The process of determining the nicotine content of a dipping bath, which consists in adding oxalic acid and tugnsten trioxide, as solids, to a sample of such bath, in the proportions of 2½ gms. oxalic acid and 5 gms. of tungsten trioxide to 50 c. c. of the bath sample and then directly titrating the resultant solution with a silico-tungstic acid solution standardized so that the silico-tungstic acid in 1 c. c. of the solution will be equivalent to 1 milligram of nicotine.

In testimony whereof, I have hereunto set my hand.

EDWIN COX.