Patented Dec. 2, 1947

2,431,672

UNITED STATES PATENT OFFICE

2,431,672

TOBACCO CONTAINING TEN PERCENT NICOTINE AS AN INSECTICIDE

Robert B. Arnold, Richmond, Va., assignor to Tobacco By-Products and Chemical Corporation, Louisville, Ky., a corporation of Delaware

No Drawing. Application November 14, 1944, Serial No. 563,444

3 Claims. (Cl. 167—34)

1

Nicotine for insecticidal purposes commonly is manufactured and sold to the consumer in the form of a concentrated solution of nicotine sulfate (about 40% nicotine expressed as alkaloid) and is applied in a variety of ways such as by simply diluting the solution and spraying it or by absorbing or distributing the solution upon a finely divided solid carrier which is applied as such as a dusting powder or in suspension in a liquid as a spray.

A variety of dusting powders containing nicotine have been described in the literature. Such dusting powders generally contain a relatively small percentage of nicotine, say 1 to 4 percent, and are suitable for direct application to vegetation but are not adapted to be transported long distances from the manufacturer to the consumers' destination due to excessive freight cost because of their weight and bulk per unit of insecticidal activity.

Prior to my present invention, the need had been recognized for a nicotine material of high nicotine content in dry powdered form. This need has been met, in part at least, by the products disclosed in my Patents Nos. 2,219,287 and 2,311,629, an essential ingredient of which products is a combination of a base exchange polysilicate such as bentonite and a salt of an alkaloid such as nicotine sulfate. In such bentonite-nicotine products about 7 to 10 percent of nicotine is chemically bonded to the bentonite and is neither volatile nor readily soluble. The particles may carry also up to about an equal amount of nicotine as sulfate absorbed or adsorbed on their surfaces but not chemically bonded thereto, this portion of the nicotine being both soluble and slowly volatile even at room temperature. Such products are satisfactory with respect to caking and are well adapted to certain uses as insecticides but are open to the objections that the portion of the nicotine combined with the bentonite is not readily available and the portion which is not combined with the bentonite is volatile and the products must therefore be transported and stored in air-tight containers. In my Patent No. 2 343,359, I have disclosed a method of meeting this latter objection by binding the soluble nicotine content of the products, i. e., that which is not chemically bonded to the bentonite, by the use of a fixing agent such as tannic acid, tobacco dust, or lubricating oil.

Another powder material containing nicotine as an essential insecticidal ingredient has been made by incorporating the nicotine into finely divided alkaline tobacco and tobacco stem material; see my prior Patent No. 2,343,360. In this product, however, the nicotine is purposely made readily volatile and the product must therefore be handled in hermetically sealed containers.

2

An object of the present invention is to provide a nicotine insecticide material in dry powder form which contains a sufficiently high percentage of nicotine to warrant long-distance shipment, e. g. 10 percent or more, preferably at least 14 percent, expressed as alkaloid, and which contains the nicotine in a readily soluble but non-volatile form, and can therefore be handled in non-sealed containers such as paper bags. Such a product must be reasonably free of the tendency to cake and must be sufficiently inexpensive to compete with other available nicotine insecticide materials. Such a product is appropriately referred to hereinafter as dry concentrate.

I have found that such a nicotine product can be provided by combining nicotine sulfate with finely divided tobacco material (leaf and/or stem) in fairly high percentage. e. g., 14% nicotine or higher, under the following conditions: (*a*) preferably use nicotine sulfate which is substantially pure or at least free from gummy or tarry material; (*b*) combine the nicotine sulfate with the tobacco material under such conditions as to produce a neutral to acid product; (*c*) combine the nicotine sulfate with the tobacco material in the presence of sufficient water; (*d*) dry the mixture of finely divided tobacco material and solution of nicotine sulfate at elevated temperature.

In the product of the present invention the nicotine sulfate is not merely carried by the finely divided tobacco material as extender nor is the nicotine chemically combined to insoluble form as in the case of bentonite-nicotine. It appears that the nicotine sulfate is converted into nicotine salts of acids that are naturally present in the tobacco material in combination with inorganic bases, which nicotine salts are soluble in water but are non-volatile, or held non-volatile by their association with the tobacco material. Whatever may be the true explanation of the fixing of the nicotine in soluble but non-volatile form in the tobacco material the invention will be described hereinafter on the basis of a chemical transformation of the nicotine sulfate by reaction with the salts naturally present in the tobacco material, it being understood that other or additional factors may be involved.

The use of pure nicotine sulfate is not essential, but it is important to avoid the presence of

any impurity which would give the product a tendency to cake.

Since the properties of the product apparently depend upon the combination of the nicotine applied to the tobacco material with the acid radicals of the salts naturally present in the tobacco material and since nicotine alkaloid is incapable of directly displacing the bases of the salts naturally present in the tobacco material, it is essential that the nicotine be applied to the tobacco material in the form of the sulfate or else that the tobacco material be first treated with sufficient sulphuric acid to combine with the bases in the tobacco material thus releasing an equivalent amount of the acids naturally present in the tobacco material to combine with the nicotine added as alkaloid, and it is desirable to provide a slight excess of such acid. Interaction of the nicotine sulfate with the salts present in the tobacco material, e. g., potassium, sodium, and calcium salts of malic, citric and other organic acids and hydrochloric acid, results upon drying in the formation of sulphates of the inorganic bases of these salts present in the tobacco material and of soluble but non-volatile salts of nicotine with the acids of the salts present in the tobacco material. Moreover, the presence of an excess of free acid in the reaction mixture safeguards against loss of nicotine by volatilization during the drying of the product, as it prevents the liberation of nicotine alkaloid by the interaction of the nicotine sulfate with constituents of some tobaccos which have a neutral to alkaline reaction. The amount of such free acid need not be rigidly controlled in order to prevent burning of foliage when the insecticide is applied to plants, since in the final product, the free acid is an organic acid or a mixture of organic acids which, even in concentrated form, does not injure foliage. The limiting factor therefore appears to be the total organic acid content of the tobacco material.

I have demonstrated that the use of sufficient water in the reaction mixture is highly important. For instance, I have found that a product, made by mixing a nicotine sulfate aqueous solution containing 40% nicotine expressed as alkaloid and 40% water with finely ground tobacco stems in proportions to yield a dry product containing about 14 percent of nicotine as alkaloid and drying the mixture at 160–170° F., still contains a small amount of nicotine sulfate; as determined by extracting the product with alcohol, filtering the extract, evaporating the filtrate to dryness, extracting the dried residue with water, acidifying the resulting solution with hydrochloric acid and adding barium chloride to precipitate the sulfate. A similar product containing the same amount of nicotine made with the use of nicotine sulfate aqueous solution containing 30 percent of nicotine expressed as alkaloid and 60 percent water and extracted and tested in the same manner was free of sulfate soluble in alcohol; while a product made in the same way by substituting an equal amount of an inert carrier material, such as pyrophyllite, for the tobacco material gave a very heavy precipitate of sulfate. Thus it is proven not only that sufficient water must be present but that tobacco material possesses an ability to bind the nicotine which is not possessed by, e. g., pyrophyllite.

My tests have shown that nicotine is quite volatile from nicotine sulfate when in the form of a thin film on an inorganic carrier; and the purpose of my present process is to convert the nicotine sulfate into other less volatile salts of nicotine or salts held in less volatile form, by the interaction of the nicotine sulfate with the salts naturally present in the tobacco. This reaction as previously stated requires non-alkaline conditions in the reaction mixture, presence of sufficient water and drying at an elevated temperature sufficient to bring about completion of the reaction.

It is important that the tobacco material forming a part of the product of the present invention be free from disease, especially tobacco mosaic, so as to prevent the transmission to other susceptible plants. While it would be possible to heat treat the tobacco material prior to using it in the present process, it is advantageous to inactivate any tobacco mosaic virus which may be present by raising the temperature of drying in the present process sufficiently high and for a long enough time to accomplish this; i. e., a moist heat temperature of 212° F. for ten minutes or more.

A temperature of 160° to 170° F. is high enough to so soften the tobacco plant fibers and other constituents that the nicotine sulfate in the presence of sufficient moisture flows or diffuses into the plant cells for the completion of the reactions, but it is desirable to initially raise the temperature of the wet mixture to 212° F. for at least ten minutes in drying. This may be accomplished by drying in the absence of air, for example by using a rotary steam tube atmospheric pressure dryer or a rotary vacuum dryer. In the latter case the wet mixture would be brought to a temperature of 212° F. under atmospheric pressure and held there for 10 minutes, when the pressure is reduced and drying proceeds at a lower temperature as is customary in such equipment.

There must be enough water present in the initial mix of tobacco material and nicotine sulfate so that, through diffusion or osmosis, the nicotine sulfate comes into intimate contact with the natural salts of the tobacco material, whereupon the acid radicals exchange. This leaves the nicotine in combination with hydrochloric, citric, malic and other organic acids. Nicotine hydrochloride is in itself non-volatile, but the nicotine salts of organic acids per se are as a rule more volatile than is nicotine sulfate. These organic acid salts of nicotine therefore appear to be acid salts or complex salts from which nicotine is not volatile or they are held within the plant cell walls or entangled in the pentosans of the tobacco material in a non-volatile form or both. Whether or not this is a true explanation of what actually happens, it seems to explain the established facts that my product contains no alcohol soluble sulfates and that the nicotine contained therein is non-volatile.

The water required may be added to the tobacco material prior to or after the addition of the nicotine sulfate solution or as a part of this solution. In adding enough nicotine sulfate solution containing 40 percent nicotine expressed as alkaloid to sufficient tobacco material to produce a final dry product containing 14 percent nicotine, enough water is contained in the mixture to cause the desirable reactions to take place to a considerable extent; such would not however be the case if a much less amount of the same nicotine sulfate solution were added to the same amount of tobacco material, say enough to produce a final product containing 3 percent or 4 percent of nicotine. I have found that sufficient water is added to the tobacco material when the nicotine sulfate solution contains 30 percent nico-

tine as alkaloid, with a corresponding larger percentage of water, and is used in sufficient amount to produce a final product containing 14 percent nicotine.

The amount of nicotine sulfate reacted with the tobacco must of course be proportioned to the natural salt content of the tobacco. I have found that when using the ground stems of flue-cured tobacco which contain a higher percentage of salts than leaf material the nicotine content of the product will be stable, i. e., substantially non-volatile at as high as 15 percent. If the nicotine content of the product exceeds about 20 percent, some of it will be found to be volatile presumably due to the fact that not sufficient salts are present in the tobacco material to react with all of the nicotine sulfate and bind the nicotine as non-volatile compounds.

It is of course within the scope of my invention to use an excess of the nicotine sulfate and to thus produce a product containing volatile nicotine along with the non-volatile nicotine. Such a product may be advantageous for certain uses. It is also within the scope of my invention to employ an excess of nicotine sulfate and to safeguard the excess against vaporization by the addition of a fixing agent as disclosed in my Patent No. 2,343,359; or, to simply add a solution of sulfuric acid to the tobacco material, then mix it with a nicotine alkaloid solution in proportional amount as suggested above. When the free sulfuric acid is added directly to the tobacco material, this should first be diluted with most of the required water. It is also within the scope of my invention to use other strong acids in place of sulfuric acid.

The product can be used alone as a dusting powder or suspended in soap solution and used as a spray and it may be used in all sorts of compositions in which it may serve to supply all or part of the insecticidal activity of the composition or all or part of the nicotine of the composition. It may for instance be mixed with extenders such as limestone flour or with various clay materials or Pyrax or with additional finely divided tobacco material or with other insecticidal agents such as cube or derris root (containing rotenone), pyrethrum, DDT, phenothiazine, calcium arsenate or with alkaline agents such as lime to liberate the nicotine in volatile form, or with copper and sulfur fungicidal agents, and the like.

The invention is illustrated by the following specific examples of the preparation of the dry concentrate:

Example I

	Pounds
Commercial nicotine sulfate solution containing 40% nicotine expressed as alkaloid and 40% water	40
Dry ground tobacco stems	76
Total wet mix	116
Moisture loss on drying	16
Dry concentrate	100

This example illustrates the least amount of water which may be used in the wet mix to induce substantially complete reaction, i. e., about 20 percent of the weight of the dry tobacco material used in the mix.

The nicotine sulfate solution and the tobacco stems are thoroughly mixed together by means of a dough mixer or a "Simpson intensive mixer," and the mixture dried by passing it through a rotary steam tube dryer which insures a temperature of at least 212° F. of the material during drying. The dry concentrate thus produced contains 16 percent of nicotine alkaloid in water soluble and non-volatile form. It is further ground to the desired fineness, and packaged for shipment in paper or cardboard containers.

Example II

	Pounds
Pure nicotine sulfate solution containing 30% nicotine expressed as alkaloid and 60% water	47
Dry ground tobacco leaf and stems	78
Petroleum lubricating oil	3
Total wet mix	128
Moisture loss on drying	28
Dry concentrate	100

In this example the amount of water used in the wet mix is about 36 percent of the weight of the dry tobacco material used, which proportion insures complete reaction. The oil is added as an insurance against caking in the package. The mixing, drying and grinding are carried out as in Example I, giving a final product containing about 14 percent nicotine alkaloid.

Example III

	Pounds
Commercial nicoting sulfate solution containing 40% nicotine expressed as alkaloid and 40% of water by weight	25
Dry ground tobacco material	85
Water	20
Total wet mix	130
Moisture loss on drying	30
Dry concentrate	100

This example illustrates the method of preparing a dry concentrate containing 10 percent nicotine by adding enough water to the wet mix independently of the nicotine solution to bring about the desired reactions. The mixing, drying and grinding are carried out as in Example I.

Example IV

393 parts by weight of tobacco dust (leaf and stem material) were thoroughly mixed with 250 parts by weight of a 13 percent solution of sulfuric acid. 100 parts by weight of an 80 percent solution of nicotine alkaloid were added and thoroughly mixed. The wet mixture was then dried at a temperature of 160° to 170° F. and lost about 37 percent of its weight as water. Very little of the nicotine content of the mixture was lost by evaporation during the drying operation. The product after grinding to a fine powder in a ball mill contained 16 percent of nicotine and some free organic acid and was a free flowing non-caking powder.

The following are examples of a few uses of the dry concentrate:

(*a*)

	Per cent
Dry concentrate (tobacco stem base), 15% nicotine	10
Ground cube root, 5% rotenone	15
Pyrophyllite (inert extender)	74.5
Vatsol (wetting agent)	0.5

Thoroughly mixed, this gives an insecticide dust containing 1½ percent nicotine and 0.75%

rotenone which is effective against many vegetable insects and European corn borer.

(b)

	Percent
Dry concentrate, 14% nicotine	20
Lead arsenate powder	20
Micronized sulphur	58
Lubricating oil	2

This mixture when dusted on apple trees at intervals during the season is a good control for codling moth and scab.

(c)

The dry concentrate (14% nicotine) used alone as a spray at the rate of 3 lbs. to 100 gallons of water, or at the rate of 1½ lbs. of dry concentrate plus ½ gallon of summer spray oil to 100 gallons of water produces an effective spray for the control of codling moth and certain other insects on apples.

(d)

	Percent
Dry concentrate (14% nicotine)	50
DDT	12.5
Pyrophyllite	37.5

The above mixture used as a spray at the rate of 3 lbs. to 100 gallons of water is a safe and effective control for codling moth on apples.

(e)

	Percent
Dry concentrate, 14% nicotine	14
Calcium arsenate powder	81
Hydrated lime (dry)	5

This is a combination dust which fits the cotton field. When applied as a dust at intervals during the growing season at the rate of 7 lbs. to 10 lbs. per acre it effectively controls both boll weevil and cotton aphis.

(f)

	Percent
Dry concentrate, 14% nicotine	29
Hydrated lime (dry)	71

Example *f* is an insecticide dust containing about 4 percent nicotine expressed as alkaloid and is a highly effective general aphicide. It constitutes an improvement in the art as heretofore practiced in that the above dry mixture is very easily made compared to mixing a liquid nicotine sulphate solution with hydrated lime, which is likewise true for all of the dry mixtures cited above; and also because there is no immediate liberation of free nicotine in the dry mixing of hydrated lime and dry concentrate. This dusting mixture, *f*, may thus be kept in bags, or even in open containers until needed. This is also true for the cotton dust, Example *e*. When such a dry mixed dust, i. e., one containing dry concentrate and a dry alkaline material such as hydrated lime, is applied to plants it takes up enough moisture from the foliage or surface of the insects, on account of dew, etc., to cause a reaction to take place liberating the nicotine from its salts as the free alkaloid which is the most toxic form for killing aphids.

I claim:

1. Process which comprises uniformly mixing finely divided tobacco material with nicotine sulfate in quantity sufficient to supply at least about 10 parts by weight of nicotine expressed as alkaloid for each 100 parts by weight of tobacco material in the presence of at least about 20 parts by weight of water to each 100 parts by weight of tobacco material under neutral to acid conditions and drying the mixture at a temperature of at least about 160° F.

2. Process as defined in claim 1 wherein the temperature of the mixture is raised to at least 212° F. for at least 10 minutes during the drying operation.

3. A new product consisting essentially of whole tobacco material and at least ten percent of added nicotine calculated as the free alkaloid on the dry weight of the tobacco material combined with the tobacco material in substantially non-volatile but water soluble state prepared by the process defined in claim 1.

ROBERT B. ARNOLD.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,731,678	Mewborne	Oct. 15, 1929
2,007,123	Dunn	July 2, 1935
2,139,340	Hunter	Dec. 6, 1938
2,228,096	Tisdale	Jan. 7, 1941
2,343,360	Arnold	Mar. 7, 1944