

# The Present Status of Cryolite as an Insecticide

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## THE PRESENT STATUS OF CRYOLITE AS AN INSECTICIDE.

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### INTRODUCTORY.

For many years arsenicals have been used as stomach poisons for the control of chewing insects. These were first discovered accidentally and at that time (about 1860) arsenic was used in a rather soluble form in spray materials like Paris Green and London Purple. In view of the injury to foliage caused by these materials and the consequent limited way in which they could be used for insect control a direct effort was made in 1885 in connection with the Gypsy Moth problem in Massachusetts to find an arsenical which was comparatively insoluble. As a result Arsenate of lead was first made and used in 1892 to control chewing insects and this was adopted as a standard material and was recommended and used almost exclusively for the control of chewing insects until the period of the world war. Then a demand was made for a cheaper arsenical because of the high price of lead. At that time calcium arsenate and other cheaper materials were manufactured. But these contained a larger percentage of water soluble arsenic than could be tolerated by plants and continued to injure foliage. In 1925 the toxic effects and the cumulative toxicity effect of both lead and arsenic upon the human body were being recognized by toxicologists.

Although the British government as early as 1903 had fixed a tolerance of 1.429 mg. of  $As_2O_3$  residue per kilogram of food stuff (equivalent to .01 grams per pound) this was practically ignored until 1925 when England threatened an embargo on American fruit. This was soon followed by the establishment of the same tolerance on both fruits and vegetables by the U. S. Pure Food and Drug Administration. Although the lead tolerance has been changed for 1934 to 0.019 grains of lead per pound, the arsenic tolerance of 0.01 grains of arsenious oxide has remained as in 1933.

In view of this situation there has been widespread search for substitutes both in the field of organic contact insecticides and in an attempt to find a good nonarsenical stomach poison.

The ideal insecticide should be a substance with a high acute toxicity to a wide variety of insects, be non-injurious to plants and have no effect upon man. This will probably never be attained since all three of these are fundamentally alike biologically. In view of the lack of such an insecticide we have been required to consider these upon the basis of their relative toxicity to man and select an insecticide which seems to be the lesser evil.

On this basis fluorine compounds have been thoroughly tested during the past few years and two especially, cryolite

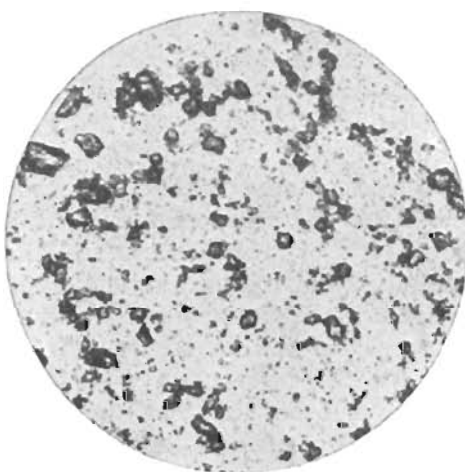


FIG. 1. Showing the variation in the size of particles of natural cryolite when ground. (Greenland.)

and barium fluosilicate, have seemed to fit more nearly the requirements and be most promising because of their margin of safety on foliage, their relatively high toxicity to insects and their relatively low toxicity to man when compared with arsenate of lead.

#### PHYSICAL AND CHEMICAL PROPERTIES.

Cryolite ( $\text{Na}_3\text{AlF}_6$ ) is one of the fluoalumates of an alkali metal. The other possible combinations are potassum hexafluoaluminate ( $\text{K}_3\text{AlF}_6$ ) Ammonium hexafluoaluminate ( $(\text{NH}_4)_3\text{AlF}_6$ ) and lithium hexafluoaluminate ( $\text{Li}_3\text{AlF}_6$ ).

Insecticides containing water insoluble double fluorides of the alkali metals with Aluminum are obtained by treating

water insoluble Aluminum compounds such as  $\text{Al}_2\text{O}_3$  with alkali metal compounds such as KOH in suspension in the presence of water and gaseous H. F. or its aqueous solution and drying and comminuting the gel thus formed (Carter 14).

Cryolite occurs in two forms, natural and synthetic. It occurs in Greenland as a native fluoride of Aluminum and sodium. More than 10,000 tons are used annually for the manufacture of aluminum, the fused mineral being used as the bath for the electrolysis of alumina to the metal. Cryolite is also used as flux in the manufacture of white Portland cement,



FIG. 2. Showing the uniformity of size of particles in synthetic cryolite. (Jungmann and Co. product.)

in the enameling of iron ware and in the manufacture of opaque white glass.

The natural cryolite when ground is a heavy powder with uneven sized particles (Fig. 1) and is therefore not well adapted to insecticidal purposes.

The synthetic powdered material is light and nearly uniform in composition (Fig. 2) and has a solubility of 1 gram to 1.639 cc. of water. It is available in commercial quantities. It contains the following chemicals:

Sodium aluminum fluoride.....	98.20%
Silica.....	.74%
Sodium sulphate.....	.36%
Iron oxide.....	.06%
Moisture.....	.64%

Both natural and synthetic cryolite are almost transparent in water suspensions. Cryolite appears soluble because the refractive indices of water and cryolite are nearly identical.

When properly washed during the process of manufacture, suspensions or solutions of these compounds in water give a practically neutral reaction and as their solubility is low they are less likely to injure or burn plant foliage than such compounds as the fluosilicates. Considering their fluorine content alone as a measure of toxicity they compare favorably with the fluosilicates and metallic fluorides which have a definite insecticidal value.

Aqueous solutions of Barium Fluosilicate have a corrosive effect upon spray pumps. In order to overcome this situation the Grasselli Chemical Company have obtained a patent (No. 1,931,367) which covers the addition to their Barium Fluosilicate of a slightly water soluble substantially neutral fluoride. Synthetic cryolite is a material of this type and can be used for this purpose.

#### THE RELATIVE TOXICITY OF SOME FLUORINE COMPOUNDS AS STOMACH INSECTICIDES.

In attempting to estimate the relative toxicity of the more important fluorine compounds Shepard and Carter (61) have determined the median lethal dose range of each material on the basis of mg. per gram. The median lethal dose of acid lead arsenate is about 0.09 mg. per gram and is given here in order that the relative fluorine toxicities as specified below may be compared on that basis:

	Solubility at 25° C. grams per 100 cc.	Medial Lethal Dosage Range mg. per gram
<b>FLUORIDES—</b>		
Sodium.....NaF.....	4.054	0.11-0.15
Manganese.....MnF <sub>2</sub> .....	.186	.20- .40
Lead.....PbF <sub>2</sub> .....	.066	.25- .40
Magnesium.....MgF <sub>2</sub> .....	.013	.57
<b>FLUOSILICATES—</b>		
Sodium.....Na <sub>2</sub> SiF <sub>6</sub> .....	.762	.10- .13
Potassium.....K <sub>2</sub> SiF <sub>6</sub> .....	.177	.07- .10
Barium.....BaSiF <sub>6</sub> .....	.025	.09- .12
<b>FLUOALUMINATES—</b>		
Sodium.....Na <sub>3</sub> AlF <sub>6</sub> .....	.061	.05- .07
Potassium.....K <sub>3</sub> AlF <sub>6</sub> .....	.158	.08- .10
Ammonium.....(NH <sub>4</sub> ) <sub>3</sub> AlF <sub>6</sub> .....	1.031	.11- .14

It will be noted from the above figures that sodium fluoaluminate or cryolite shows the lowest range median lethal dose and is therefore practically twice as toxic relatively as arsenate of lead.

#### COMPATIBILITY OF THE FLUOSILICATES AND CRYOLITE WITH ARSENICALS.

The use of combined arsenates and fluorine compounds has been suggested in the hope that additional insect control might be secured and that the arsenical residue might also be reduced.

Carter (11) has published certain data concerning these combinations. He finds that fluosilicates in solution have an acid reaction and in general are much more soluble than the arsenates used in insect control. In solution they are used at the rate of 1 pound each to 45.8 gallons of water. Severe injury to vegetation may be caused by excessive amounts of soluble arsenic or by solutions having an acid reaction. The solutions were analyzed for both of these factors and he found that with lead arsenate there seemed to be a tendency for the fluorine compounds to form less soluble arsenic than is formed in tap water alone. The other fluosilicates and other arsenates were largely decomposed. The presence of cryolite decreased slightly the amount of soluble arsenic formed by all the arsenates used in these experiments. Barium fluosilicate caused the formation of smaller amounts of soluble arsenic than the fluosilicates of sodium, potassium or calcium. This was probably due to its lower solubility. Cryolite gave a low acidity reaction with all the arsenates tested and it also showed a low soluble arsenic content when mixed with these materials.

#### COMPATIBILITY WITH FUNGICIDES.

It is frequently necessary to mix insecticides and fungicides together in the same spray in order to control insects and plant diseases. Marcovitch has mixed cryolite at the rate of 1½ pounds to 50 gallons of water in a lime sulphur spray at the rate of 1 to 40 without causing injury. When used at the same strength with Bordeaux mixture 3-3-50 no foliage injury was caused. Fish oil at the rate of 1 pound to 4 pounds of cryolite may be used safely as a sticker and greatly improves the adhesive qualities of the spray.

## PLANT INJURY OR BURNING.

Many types of chemicals cause foliage injuries when used as dusts or sprays. As a rule more injury is caused by the material in spray form and in general materials that are readily soluble in water are more apt to burn. On the other hand a highly insoluble material usually shows poor toxicity and is not a good insecticide. The margin of safety between a good insecticide and a safe material upon plants is so small that only a few known chemicals even approach the required specifications. Cryolite with a solubility of 1-1639 and barium fluosilicate with a solubility of 1-3750 have proven relatively safe on foliage by tests conducted to date and have shown a rather high degree of toxicity to insects. When used as a spray upon bean foliage at the rate of 2 or 3 pounds to 50 gallons, Howard, Brannon and Mason have shown they produce no injury. When used as a dust at the rate of 6 to 12 pounds per acre Marcovitch has shown there is no injury to bean or potato foliage, but that injury occurred when amounts greater than 20 pounds per acre were used.

According to Marcovitch different plants will vary regarding their susceptibility to burning by fluorine compounds. Cotton seems to be the most resistant, followed by beans, cabbage, apple, potato, tobacco, cucumber, peanuts, peach and smartweed. The latter is unusually sensitive to fluorine compounds.

Various workers attempting to control several different insect pests have found cryolite safe to most foliage in general. Specific reference is made to these findings in several places under specific insects mentioned in the following discussion.

Barium fluosilicate is considered safer than cryolite by some investigators, but according to Dr. N. F. Howard, burning resulted in several instances on bean during 1933 with Barium fluosilicate and W. L. Brannon found dahlias injured by the same material during 1933.

## POISONOUS EFFECTS OF FLUORINE ON MAN AND ANIMALS.

When fruits and vegetables are sprayed with fluorine compounds and ingested how poisonous are they to man? This question has been variously answered by different workers. There is reason to believe that cryolite and barium fluosilicate are less toxic than sodium fluosilicate. Experimental work by Sollman and others working with animals which were fed

sodium fluosilicate in large doses indicates that the soluble arsenicals such as sodium arsenite are nine times more toxic than sodium fluosilicate.

Marcovitch has stated (44) that according to Gautier and Clausman the average spray residue of fluorine compounds contain less than 3 parts of fluorine per million of food stuffs while natural foods contain on the average 26.5 parts of fluorine per million. Since therefore we are apparently consuming more fluorine in our daily diet than would be possible from the consumption of fruits and vegetables sprayed with fluorine, these sprayed materials should offer no additional health hazards.

Both fluorine and arsenical compounds have high acute toxic values as indicated by the following figures (Marcovitch 44).

Acute toxicities (from Kuhn (Trans. Fourth Int. Ent. Congress 1928) and Muehlberger (Jour. Pharm. & Expt. Ther. 1930).

M. L. D.

Calcium arsenate.....	38 mg. per Kilo (dogs).	Kuhn.
Lead arsenate.....	500 mg. per Kilo (dogs).	Kuhn.
Lead arsenate.....	75 mg. per Kilo (rabbits).	Muehlberger.
Sodium fluosilicate.....	150 mg. per Kilo (dogs).	Kuhn.
Sodium fluoride.....	200 mg. per Kilo (rabbits).	Muehlberger.
Barium fluosilicate.....	175 mg. per Kilo (rabbits).	Muehlberger.
Cryolite.....	500 mg. per Kilo (not fatal).	Marcovitch.

In considering the residue problem we are primarily concerned with Chronic toxicities. According to Marcovitch the fluorine compounds are at least 100,000 times safer than lead arsenate in this respect, and possess a marginal safety factor over the average spray residue content of 75.

The situation in California is apparently considered in the same light if we may judge from the following quotation taken from the 1931 Annual Rept. of the Calif. Agr. Exper. Sta., concerning the problem of fluorine spray residues. "From a number of chemical analyses made by the Bureau of Chemistry at Washington, D. C., it would seem that on vegetables which are washed before marketing, there is not sufficient residue to be dangerous for human consumption even though dusted excessively."

On the other hand Carter (13) states that in the Pacific Northwest where there is very little rain during the growing



season and where as many as 6 or 7 sprays are applied ranging from 2 to 4 pounds per 100 gallons of water during each application, the spray residue builds up to a considerable amount especially when oils are used. Under these conditions, the spray residue on fruit has run very high, but fluorine compounds do not leave as much residue on sprayed fruits as arsenical sprays. However when oils are used considerable residues result. The maximum found when barium fluosilicate was used was 0.927 grains of barium fluosilicate per pound of fruit. This is equivalent to 53.9 parts per million. Normal spraying however usually shows 0.15 grains of barium fluosilicate per pound (equivalent to 8.7 parts per million. Washing usually leaves about 2.1 parts per million. Cryolite contains 1.3 times as much fluorine as barium fluosilicate.

Investigators have differed considerably regarding the use of fluorine in one form or another when fed to or injected in man and animals. Baldwin (2) and McNally (40) have reported several cases of fluorine poisoning in man. Blaizot (5) Wieland and Kurtzohn (77) and Marcovitch (45) studied the lethal doses of different forms of fluorine for rabbits. Heidenhain (31) has reported on the lethal effects of sodium fluoride in dogs. By using sublethal doses of fluorine in different forms, Sollmann, Schetter and Wetzel (69) Bergara (4), Shultz and Lamb (60) and McClure and Mitchell (38) observed an impairment of growth and feed consumption in rats.

Several investigators have studied the effects of fluorine on the different organs and tissues of the body. Brandl and Tappeiner (9) could find no histological changes in the blood, liver, kidneys or muscles of a dog fed varying amounts of sodium fluoride. The same investigators found no evidence of histological change in the bones. Sollman, Schettler, and Wetzel (69) were unable to find histological lesions in rats fed 8 mg. of sodium fluoride per kilogram of body weight daily for 9 weeks. Pitotti (51) observed a degeneration of the epithelium of the kidneys and a cloudy swelling of the liver in rabbits and guinea pigs fed lethal doses of sodium fluoride. Weinland (76) reported that the mucous membrane of a frog was killed by a 2.1 per cent solution of sodium fluoride. Goldemberg (23) reported that the feeding of sodium fluoride caused an increase in the size of the thyroid glands of dogs and rats, but these results could not be verified by Chaneles (15) and Tolle and Maynard (74).

Several investigators, Schulz and Lamb (60) McCollum, et al (39) Bergara (4) and Tolle and Maynard (74) have shown the specific effect of fluorine on the teeth of rats. The incisors became soft, elongated, and lost their normal pigmentation. The teeth of dairy cattle also became soft and showed excessive wear when rock phosphate containing fluoroine was fed according to Taylor (73) and Huffman and Reed (33). The effect of fluorine ingestion on human teeth when obtained in water supply has been reported by Smith, Lantz and Smith (63, 64 and 65).

They found that mottled enamel of the teeth is endemic at St. David, Ariz. and has been produced in experimental animals by water from that region. Chemical examination of the water showed the presence of 3.6—7.15 mg. of fluorine per 1 of water while water from non endemic localities gave 0—0.3 mg.

The production of mottled enamel is attributed to the ingestion of fluorine in water and not to the food supply. The source is apparently rock phosphate and black mica both of which contain 3-5% of fluorine. Concentrations of fluorine above 2.7 parts per millinon were definitely toxic when ingested with drinking water.

Several investigators have attempted to find the effect of fluorine feeding on bone formation chiefly by using rock phosphate as a mineral supplement in animal nutrition. Hart and his associates (30) reported improved bone formation when rock phosphate was used to supplement low phosphorus rations for pigs. On the other hand Forbes and his coworkers (19) found that the feeding of rock phosphate to pigs produced less dense and weaker bones than when no minerals, or minerals practically free from fluorine, were fed. The weaker bones were characterized by maximum magnesium and phosphorus content and minimum calcium and carbon dioxide percentages. Reed and Huffman (52) demonstrated that the feeding of rock phosphate resulted in the thickening of the jaw and the metatarsal bones of dairy cattle. The work of McClure and Mitchell (38) showed an increase in the ash percentage of bones, accompanied by a slight decrease in the calcium content of the ash, in rats on high fluorine rations. Contrary to this work Tolle and Maynard (74) showed a decrease in the percentage of bone ash in rats fed a ration containing 1.8 per cent rock phosphate. They furthermore reported that

phosphatic limestone, containing approximately 1 percent fluorine was equal to a mixture of limestone and steamed bone meal for growth and bone formation in the pig.

McClure and Mitchell (38) found that fluorine in the form in which found in rock phosphate; namely, calcium fluoride, depressed calcium metabolism in the pig and that excessive fluorine intake also decreased growth and feed consumption.

Fluorine is a normal constituent of body tissues. This has been shown by Zdarek (80) Gaatier (22) Wrampelmeyer (79) Joblbauer (34) Harmes (29) and Sonntag (70).

Kick, Bethke and Edgington (36) have recently compared the feeding of fluorine salts with the natural mineral when each was used in comparable feeding experiments. They found growth impaired, bones weakened, teeth softened, and similar physiological effects were produced in swine by both materials. Rock phosphate however produced certain pathological changes in the kidney which sodium fluoride did not produce.

The recent work of Phillips, Alvin, Hart and Bohstedt (50) gave evidence to show that chronic fluorine poisoning does not inhibit reproduction in the rat and therefore any unfavorable effect upon reproduction arises secondarily as the result of a systematic reaction to fluorine. No clear cut and positive evidence is available to show that chronic fluorine poisoning has a cumulative effect upon reproduction or other physiological processes from generation to generation for as long as 5 generations.

The most striking thing about the experimentation with fluorine compounds upon animals is that the results obtained by apparently equally competent workers are highly contradictory which indicates that certain factors other than fluorine may have caused these differences. Also these workers have assumed that fluorine regardless of its source or condition should produce the same effect upon animal tissues whether ingested with water or food or injected into the body with a needle. Furthermore the changes which might take place due to the medium of the plant as is known to occur in the case of certain other chemicals used upon plants has not even been considered. It has been definitely demonstrated by field work that sodium fluoride and sodium fluosilicate are too soluble and too injurious to plants to be used generally in a

practical way, but that cryolite is insoluble and safe on plant foliage. Probably the same difference is to be found in the case of man but practically all of the experimental work performed to date has been done by using the soluble form, sodium fluoride. These experimental data as such are not applicable to the insoluble materials. It should be stated also that the European laws have already differentiated distinctly between 1, acid fluorides such as Ammonium bifluoride and Sodium bifluoride which are considered highly poisonous; 2, soluble neutral fluorides such as Sodium fluoride and Sodium Silica Fluoride which are held as mildly poisonous; and 3, the insoluble fluorides such as Synthetic cryolite which is considered as non-poisonous.

It should be borne in mind that the main question is the form in which fluorine appears. If the fluorides were as poisonous as to justify the tolerance dosage of 0.01 gram per pound of fruit, it would be impossible to manufacture cryolite under present conditions as the workmen are obtaining many times that amount during each production without having ever suffered injury to their health. Competent authorities also point to the fact that Calcium Fluoride which is similar to cryolite is generally and extensively prescribed in medicine. Also enamel and similar wares are used extensively which average a cryolite content of 10% and neither of these sources have been considered dangerous to human health.

In order to determine the relative toxicity of materials which cause acute poisoning or chronic intoxication in man it is necessary to experiment with as many forms of lower animals as possible and then assume that the toxicity in the case of man is no lower than in these experimental animals. Different materials may also cause different symptoms in the same species of animal so that loss of hair or other similar conditions may preclude more marked symptoms. If comparisons must be made, uniformity of experimental conditions should be adhered to. This apparently has been done in the case of the feeding experiments conducted by Smyth and Smyth (66).

They have published comparative toxicity data showing that the fluorine compounds are less toxic than lead arsenate. These experiments were apparently well planned and the best controlled of those dealing with fluorine compounds. They compared the relative toxicity of fluorine and arsenical insecticides by means of feeding experiments conducted on white

rats for a period of 16 weeks. As a basis for comparison they used behavior, appetite, fecundity, growth, tooth development and abnormality and organic pathology, and all of their data indicated that arsenical compounds are several times more toxic than fluorine compounds. According to their work the use of fluorine insecticides leaves a much wider margin of safety than the use of arsenical materials based on the relative weight of spray residue to the fruit and the consequent amount toxic to the consumer. These conclusions should probably be considered as a more conservative estimate.

There is still some doubt concerning the question of ingestion of small amounts of fluorine or arsenic. The data available indicate that the extremely small amounts of arsenic that may be found on sprayed fruits are harmful when administered over a period of six months. On the other hand the continued feeding to guinea pigs of sodium fluoride in small amounts such as may be found on sprayed apples, appeared harmless even after several years. It seems therefore that the poisonous nature of fluorine compounds in small amounts that may occur on sprayed fruits is negligible from the standpoint of human health as far as conclusive data are available.

#### RESULTS OF EXPERIMENTAL WORK IN THE CONTROL OF INSECT PESTS.

During the past four years cryolite and several other forms of fluorine have been used extensively to test their effectiveness in controlling some of the most important pests of fruits and vegetables, especially in the United States and other agricultural areas. Three things have been sought especially.

1. A non-arsenical substitute for lead arsenate and other arsenicals.
2. A material which gave a high toxic value in controlling insects.
3. An insecticide which gave very slight or no foliage injury.

A brief summary of some of the results obtained by various workers on specific insect problems is cited here. Although both natural and synthetic cryolite have been used in these experiments, the greater part of this work has been performed with a synthetic cryolite known as Syncrolite and manufactured by Jungmann and Co.

*The Codling Moth (Carpocapsa pomonella).*

The Codling moth is probably one of the most difficult insects which the grower has to control at the present time, and the spray residue problem of lead arsenate has presented a puzzling situation. Newcomer (46) has found in his experiments at the Washington State Experiment Station that certain fluorine compounds are as effective as lead arsenate in the control of codling moth on apples in the arid regions of the Pacific Northwest. Three or four of these compounds have given rather satisfactory results. Cryolite and Barium fluosilicate are two of this number which are available and suitable for use. At present the cost of cryolite is slightly higher than lead arsenate. But it does not injure the plant nor does it affect the color, size or quality of the fruit. Furthermore the fluorine residues are easily removed with alkaline washes. They can be used satisfactorily in the second brood sprays (5th and 6th cover) at the rate of 4 pounds to 100 gallons of water combined with one pint of fish oil, or 3 pounds to 100 gallons of water with one gallon of summer oil.

In later investigations (47) he found that after July instead of oil being used with lead arsenate, cryolite may be used at the rate of 3 pounds to 100 gallons of water. In 1931 cryolite proved very effective and in some cases more so than lead arsenate.

Webster, Marshall and Hansburg (75) working in the same area found that arsenates with oils gave heavy residues but good control of codling moth. They also state that spraying throughout the season with 3 pounds of natural cryolite to 100 gallons of water plus one quart of fish oil gave slightly better results than the normal lead arsenate sprays.

Gross and Fahey (24) have reported synthetic cryolite to have marked insecticidal properties for codling moth, but its effectiveness decreases more rapidly than that of lead arsenate.

Barrett working in California (3) has carried on experiments for the control of the codling moth on Walnuts. He found that barium fluosilicate and synthetic cryolite are the only fluorine compounds of those tested (including a large series) which show promise for use in controlling this pest on Walnut. Used as a dust at the rate of 35% with 65% of a 400 inch mesh Talc each gave good results. Each gave about 90% control and neither gave foliage injury.

Pettey (48) working in South Africa found that in cases of severe infestation of codling moth lead arsenate at the rate of  $1\frac{1}{4}$  pounds in 40 gallons of water applied fortnightly throughout the season is not satisfactory as a control for codling moth. If the arsenate of lead is doubled more satisfactory results are obtained in control, but the residue is difficult to remove. In using an artificial cryolite from Germany at the rate of 2 pounds with  $\frac{1}{4}$  pint of fish oil in 40 gallons of water and applied at intervals of 3 weeks throughout the season he obtained more satisfactory results than with a similar normal program of lead arsenate alone. In addition it appeared to reduce infestations of mealy bug (*Psuedococcus maritimus*) considerably.

At a later date (49) he stated that artificial cryolite was not as effective as lead arsenate in controlling Codling Moth in Highveld orchards, but it caused no foliage injury, whereas the arsenate sprays did considerable damage. The results indicated that cryolite is more effective in control in arid summer coastal regions than in those where summer rainfall occurs.

Joubert (35) working in South Africa found in 6 of 7 comparative experiments that cryolite sprays used at the rate of 2 pounds to 40 gallons gave them from 3 to 25 per cent better control of codling moth on pears than Lead Arsenate sprays.

The fruit growers in the North West depend upon using cryolite and similar fluorine compounds for the early season sprays, because when lead arsenate alone is used for all seven or more sprays it is impossible to prevent the lead arsenate residue from becoming greater than the tolerance limits (.014 gms. for lead and .01 gms. for arsenic).

*Experiments on peach for the Control of Oriental Fruit Moth  
(Clydia (Laspeyresia) molesta Busk) and the Plum  
Curculio (Conotrachelus nenuphar Hbst).*

The foliage of the peach is usually sensitive to arsenate of lead which has been used for plum curculio and the residue problem is difficult to overcome. Defoliation of the tree has always been a problem with arsenate of lead. In 1929 Swingle (72) showed that arsenic was found to act as a cumulative poison within the peach leaves. Acid lead arsenate when used alone in proportions of 1 pound to 50 gallons caused very

severe injury even when soluble arsenic was as low as .04% as arsenic pentoxide.

Snapp (67) used sodium fluosilicate at the rate of 2 pounds to 50 gallons and found it very toxic to curculio but also to the fruit and foliage of the peach.

Subsequently, Marcovitch, Stanley and Anthony (43) found in experiments performed in Tennessee that cryolite sprayed plots showed no trace of injury. In 1929 and in 1930 as many as 7 spray applications did not give the slightest degree of burning at the rate of one pound to 50 gallons.

Barium fluosilicate was about as safe as cryolite but with fish oil soap gave defoliation. The curculio was controlled equally well with arsenate of lead and cryolite while the oriental fruit moth was controlled better with cryolite. The cryolite sprayed plot also showed a noticeable reduction of *Bacterium pruni* (bacterial disease of peach) and thus exhibited bacteriocidal properties. The more rapid insecticidal action of cryolite and barium fluosilicate is shown by the fact that 100% mortality results in two or three days when curculios are fed upon foliage treated with these fluorine compounds while arsenate of lead treated foliage upon which they fed did not cause 100% mortality for two or three weeks time.

After obtaining a complete defoliation with 4 arsenate of lead sprays Marcovitch and Stanley working in Tennessee (45) used barium fluosilicate and cryolite as substitutes for arsenate sprays in controlling the Oriental fruit moth and plum curculio on peach. They found that dusts were not as satisfactory as sprays, largely due to weather conditions and that four sprays of cryolite and sulphur gave satisfactory control of both pests.

Snapp and Thomson (68) working in Georgia on peach report that synthetic cryolite at the rate of 2 pounds to 50 gallons caused no injury to foliage or budwood and gave almost as good control as potassium fluosilicate. Cryolite was the least toxic of the three fluorines used and potassium fluosilicate was the most toxic. Wettable sulphur apparently increases the toxicity of these fluorine compounds.

Frost of Pennsylvania obtained unfavorable results by using Sodium aluminum fluoride for oriental fruit moth on peach at the rate of 3 pounds to 100 gallons of water. He states that considerable burning resulted and a high percentage of control was not obtained as it ranged from 37% to 80%.



*The Walnut Husk Fly (*Rhagoletis completa* Cress).*

The walnut husk fly is probably one of the two or three most serious pests of the walnut industry in California. It has been introduced rather recently. Boyce (6, 7, 8) has been working on this project and making rather extensive control investigations during the past three or four years.

In 1930 the arsenicals tested were effective in causing insect mortality but all except the basic arsenate of lead caused foliage injury. The speed of their toxic action bears a direct relationship to their arsenic content and degree of solubility in water. During the same season cryolite in dust and spray form gave practically as good results as barium fluosilicate,

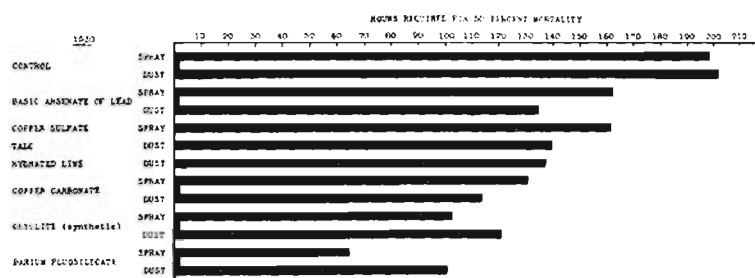


FIG. 3. After Boyce, Monthly Bull. Dept. Agr. Calif. 20: 686, 1931. Results of toxicity studies in 1930, showing number of hours required to bring about 50 percent mortality of adults in *Rhagoletis completa* Cress. Data based on average of 55 experiments in which a total of 1,944 flies was used. Average of 35 flies per experiment.

but nothing else proved as satisfactory as these two materials (Figs. 3, 4, 5). Both were safe to use on plants. The speed of toxic action is correlated with the solubility of the material in water, the more soluble producing the more rapid lethal action. Calcium fluoride and calcium fluosilicate were not effective.

The results obtained the next year showed that cryolite and barium fluosilicate exhibited similar speed of toxic action and gave better results than the other materials tested. In speed of action natural cryolite was considerably inferior to the synthetic cryolite in these tests.

Later results (1932) showed that all of the arsenicals used (acid lead arsenate, basic lead arsenate, calcium arsenate, magnesium arsenate, manganese arsenate, sodium arsenite) except basic lead arsenate caused foliage injury and this one

was consistently slowest in speed of lethal action. Boyce makes the following statement, "of the fluorines tested sodium fluoaluminate (cryolite, synthetic) barium fluosilicate and potassium fluoaluminate were the most promising from the point of view of toxicity to the insect and tree tolerance." The accompanying diagram (Fig. 6) published by Mr. Boyce shows that these three were most effective in the order named, cryolite

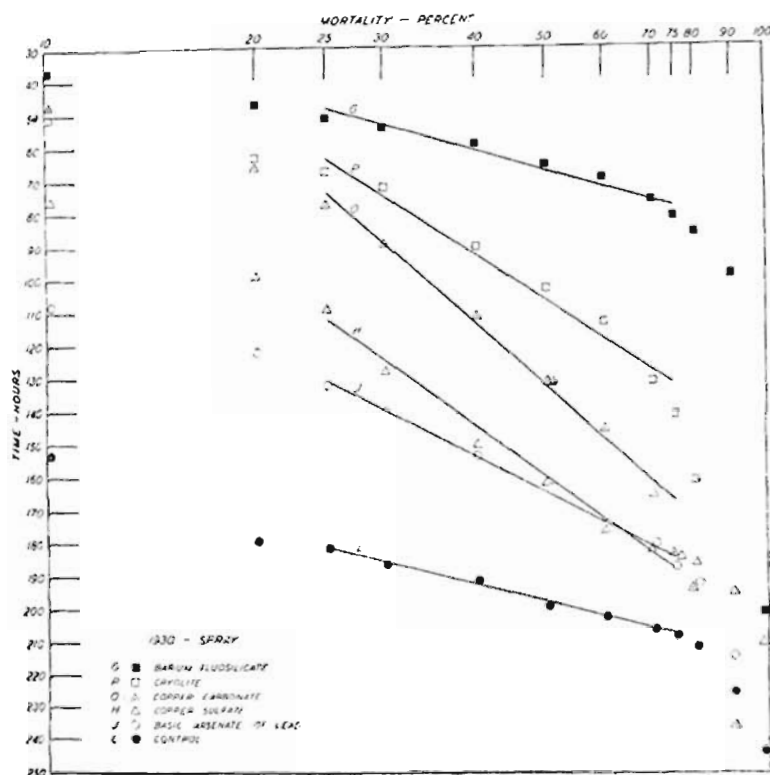


FIG. 4. After Boyce, Monthly Bull. Dept. Agr. Calif. 20: 687, 1931. Graphs showing relative effectiveness of various materials applied as sprays in 1930. The standard of comparison is the mean mortality period from 25 to 75 per cent. Data based on 55 experiments as in Fig. 3.

undiluted, giving the best results of the three and when used with mineral oil the toxicity was increased.

A dust combination of synthetic cryolite 20 pounds, Talc (fiber) 75 pounds and mineral oil 5 pounds gave 97.3% control, the highest obtained on any plot.

Synthetic cryolite and barium fluosilicate were tested extensively and although both are quite low in adhesive qualities the incorporation of fish oil, vegetable oil or mineral oil rendered them satisfactory in this respect. Of these the mineral oil proved most desirable.

In preparing a dust material, when diatomaceous earth is used as a diluent it has the decided advantage of being very light and bulky and the incorporation of oil for adhesive purposes does not affect its dusting qualities.

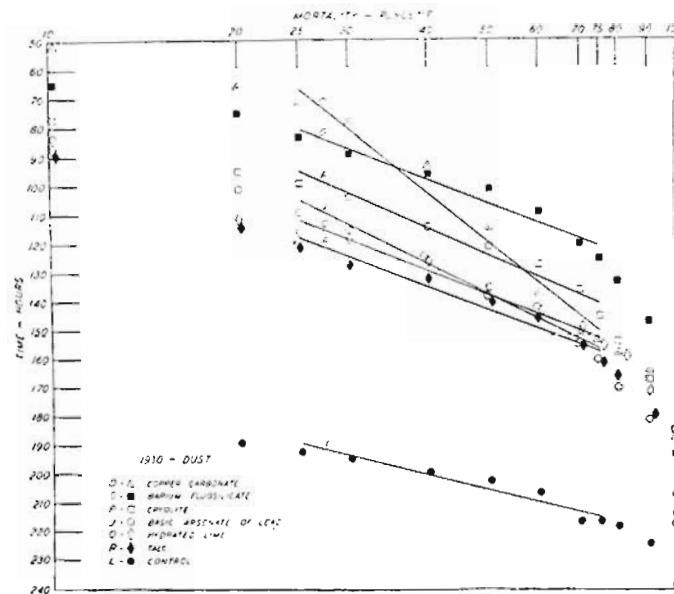


FIG. 5. After Boyce, Monthly Bull. Dept. Agr. Calif. 20: 688, 1931. Graphs showing relative effectiveness of various materials applied as dusts in 1930. Standard of comparison and data of 55 experiments as in Fig. 4.

Mr. Boyce states that "satisfactory control of the walnut husk fly may be obtained through the use of synthetic cryolite (97+ per cent sodium fluoaluminate) or barium fluosilicate" and recommends the following formulae:

1. As a spray:

Cryolite (synthetic) or barium fluosilicate, 3 pounds.  
Mineral oil (95 seconds viscosity, 90% unsulfonatable), 1 quart.  
Water, 100 gallons.  
Use from 30 to 40 gallons per average sized walnut tree. This affords satisfactory coverage.

## 2. As a dust:

Cryolite (synthetic) or barium fluosilicate, 30 percent.

Diatomaceous earth, 65 percent.

Mineral oil (95 seconds viscosity, 90% unsulfonatable), 5 percent.

The dust method is more economical.

*The Natal Fruit Fly (Pterandrus rosa).*

Similar results to those obtained by Boyce were obtained by Ripley and Hepburn (54) in toxicity studies dealing with the Natal Fruit Fly (*Pterandrus rosa*). They also found that in speed of action, natural cryolite was considerably inferior to the synthetic cryolite. The synthetic material

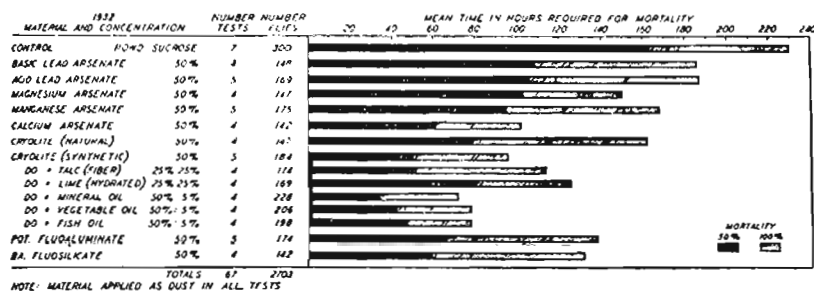


FIG. 6. After Boyce, Jour. Eco. Ent. 26: 821, 1933. Results of toxicity studies in 1932, showing relative mortality of various materials in comparison with different combinations of synthetic cryolite.

may be more effective because the bond between the elements of the molecule is not as great as in the natural product, thereby liberating the fluorine more readily.

*Grape Berry Moth.*

Runner (59) experimenting in Ohio found that cryolite and Potassium fluoaluminatate failed to control the grape berry moth and in some cases caused injury to the grape and also to certain vegetables.

*The Apple Curculio (Tachyterellus quadrigibbus).*

Hammer of New York (28) carried on experiments to control this pest and found that cryolite used at the rate of 6 pounds to 50 gallons of water gave a high percentage of control (74 dead and 3 alive out of 100 released). Also he liberated curculios on a caged tree sprayed with cryolite and found only 12 apples out of 533 were injured by feeding. Lead arsenate gave slightly better control.

*The Mexican Bean Beetle—Epilachna Corrupta.*

Since the bean plant is quite sensitive to the effects of arsenate of lead and is easily injured, it has been difficult to secure a material which would give high toxicity of bean beetle without injuring the plant. For several years Magnesium arsenate has been recommended and used as a control measure but magnesium arsenate is not a generally used insecticide and is consequently difficult to obtain in many states or regions where the bean beetle is a pest.

Howard, Brannon and Mason (32) of the United States Dept. of Agriculture Bureau of Entomology working in Ohio and Virginia have used fluorine compounds rather extensively over a three year period as substitutes for the arsenicals. They have found sodium fluosilicate to be too injurious to bean foliage and not sufficiently toxic to kill the insect. On the other hand synthetic cryolite proved very effective for controlling this pest and increased the yields in the great majority of the experiments appearing to be beneficial to the bean plant. Under conditions of light infestation when used at the rate of 1 pound to 50 gallons and 2 pounds to 50 gallons excellent results were obtained. When used under conditions of heavier infestations at a strength of 1 pound to 50 gallons it was not as good as Magnesium arsenate at the same strength, but at the rate of 2 pounds to 50 gallons it gave equally good results as Magnesium arsenate at the same strength. When used at the rate of 3 pounds to 50 gallons results were sometimes better than magnesium arsenate 2 pounds to 50 gallons. As a dust it is not entirely satisfactory but gave better results than an 80 per cent barium fluosilicate used under the same conditions.

Cryolite is apparently less injurious to foliage and safer than Magnesium arsenate especially in dry seasons and may in the near future be recommended by scientific workers in preference to it because of recent injury and lack of toxicity encountered in using magnesium arsenate and because cryolite is becoming more generally used and is available in most agricultural areas.

*The Maize Stalk Borer (Busseola fusca Fall).*

This pest is important in South Africa and has been studied by Ripley and Hepburn. They report (53) that cryolite gave

satisfactory control of the stalk borer as a spray at a 1-600 (by weight) strength. Although causing slight burning to the plant, it had the advantage over derris products of being a stomach poison and larvae need not necessarily be hit by it in order to be killed. It is also cheaper than derris products. In a later paper (55) they reported that cryolite when used on maize at the previously recommended strength and where 75 per cent of the stalks were infested even when applied a week late gave sufficient control of stalk borers to increase the yield of grain 26 per cent by weight. Cryolite being non-volatile remains in the plant until washed out by rain and when soap is added at the rate of 1 pound to 20 gallons the penetrating power and toxicity are increased. Synthetic cryolite appears to be the most satisfactory stomach poison, although contact insecticides like derrisol have given good results and are recommended.

*A Garden Caterpillar (Polia (Mamestra) Oleracea).*

Speyer (71) made tests with various materials including several fluorides in an attempt to control a garden caterpillar (*Polia (Mamestra) Moleracea*). Arsenate of lead cannot be used on tomatoes in bearing. Sodium fluoride injured the foliage. Barium fluosilicate had no effect on the larvae and no injury to the foliage. Aluminum silica fluoride was toxic to the larvae and did not injure foliage but the cost was too high. The most satisfactory results were obtained with synthetic cryolite in the form of a very fine powder used at the rate of 6 pounds to 100 gallons of water with the addition of 2 ounces of saponin as a spreader. The action may be largely a contact.

*The Wattle Bagworm (Acanthopsyche junodi Heyl).*

Ripley and Petty (56) worked with dust materials in an attempt to control the wattle bagworm in South Africa. Field and laboratory results on the basis of relative toxicity show them to be in the following order, the most toxic first:

1, Paris Green; 2, Sodium ferric fluoride; 3, Sodium fluosilicate; 4, Natural and synthetic cryolite; 5, Calcium arsenate; 6, Barium fluosilicate; 7, Calcium fluosilicate; 8, Schweinfurth yellow; 9, Copper carbonate.

Although showing greater toxicity the first three of these are usually dangerous from the standpoint of foliage injury while cryolite which gives a high toxic value among this group

is safer than any in the list with the possible exception of barium fluosilicate and certainly much safer than the first three.

*Grasshoppers.*

In using cryolite as a toxic material in grasshopper baits, Richardson and Thurber (57) found cryolite was not as toxic as arsenate of lead. The work of Marcovitch (41) also showed that cryolite gave rather poor control in the form of a bait.

*Turnip webworm (Hellula undalis F.).*

Robinson of Alabama (18) working on this pest showed that cryolite was effective in killing all the larvae of this species under experimental conditions.

*The Tobacco Hornworm. (Protoparce quinquemaculata).*

Marcovitch and Stanley (42) used lead arsenate, cryolite, barium fluosilicate and potassium fluosilicate in comparative tests against tobacco hornworms and found cryolite to give almost complete control of this pest with lead arsenate and barium fluosilicate giving almost as good control in the order named.

*Shade Tree Pests.*

*The Bagworm (Thyridopteryx ephemeraiformis); The Fall Webworm (Hyphantria cunea); and the White Marked Tussock Moth (Hemerocampa leucostigma).*

Tests made upon these three very important shade tree pests in Ohio by the author have shown that they can be very effectively controlled by Cryolite and without injury to the foliage of the Maples, Elm, Oak and other common shade trees and ornamentals which these usually attack. (Unpublished data.)

CONCLUSIONS.

The foregoing summary of literature and experimental work would indicate that:

1. Synthetic cryolite is superior to natural cryolite and in view of its physical and chemical properties is well adapted to insecticidal work.

2. Experimental work has indicated that cryolite has a relatively high toxicity to insects and gives the minimum of plant injury when properly used.

3. Fluorine when added in chemical form to food materials or injected into body tissues has given indication of chronic effects but other experiments conducted in a similar manner have given contradictory results. Also there is no available data regarding the effects of fluorine when plants sprayed with materials containing it were used as the source of food. Furthermore all experimental work to date has been performed with the soluble neutral fluorides and there is no data available upon the use of the insoluble fluorides although tolerance figures are placed upon these latter materials upon the basis of experimentation with the more soluble forms.

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