Table VI.
 Relationship Between Position of a Methyl Group and Toxicity to Two-Spotted Spider Mites



due to chlorine is roughly equivalent biologically to the same increase due to an alkyl radical.

As in the long-chain alkyl series, there is a nice relationship between structure and activity in the aryloxy alkyl sulfites.

Table VII. Effect of Ring Substitution on Toxicity to Two-Spotted Spider Mites in a Series of Aryloxyisopropyl 2-Chloroethyl Sulfites



From the simplest member of the series to the most active there is approximately a 125-fold increase in activity. Many other types have been tested; although many are very toxic to mites, none is more toxic than 2-(p-tert-butylphenoxy)isopropyl 2-chloroethyl sulfite, which is marketed commercially as Aramite (7).

$$(CH_3)_3C$$
---OCH<sub>2</sub>CH-OSO---CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl

The great activity of this compound on many species of mites, coupled with its low toxicity to predatory insects, its low mammalian toxicity (oral  $LD_{50}$  for rats and guinea pigs, 3.9 grams per kilogram of body weight), its high ovicidal activity, and its safety on plants makes it an ideal miticide.

While many sulfites are extremely toxic to the two-spotted spider mite, many others are not. Almost any of the simple symmetrical ones which a chemist would tend to try first are so inactive that they would not pass a Table VIIII.Effect of Ring ChlorineSubstitutionofAryloxyisopropyl2-ChloroethylSulfitessonToxicitytoTwo-SpottedSpiderMites



screening test. Some others which are active cause injury to a wide variety of plants at the dosage required to kill mites. It is, therefore, necessary to try several members of a series before a valid conclusion can H<sub>2</sub>Cl be reached.

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# **RODENT CONTROL** A Review of Chemical Repellents for Rodents

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E MPHASIS ON CHEMICAL REPELLENTS as a means of reducing damage by rodents and other animal pests has been increased in recent years, though the deterrent approach to rodent control is not new.

The need for such protective materials is generally recognized. It has been estimated that the annual economic loss due to rats and other rodents in the United States may amount to between one and two billion dollars. Part of this is loss to orchards, field crops, poultry, and other farm products, part is loss to buildings and equipment, and a considerable portion involves damage to or contamination of packaged goods in transit or storage.

The most satisfactory method for preventing these losses would be the elimination of the rodent populations through extermination campaigns and by use of rodent-proof construction. The importance of these measures cannot be minimized and every effort should be made to increase their application where feasible. However, such methods may not be completely successful in all cases and may be impossible or impractical to carry out in the vicinity of temporary storage dumps or the wharf areas of large ports. The supplementary use of rodent-repellent containers would be of material advantage in reducing the economic loss due to rodent depredations on packaged goods.

Although there is a definite relationship between the physical hardness or toughness of a barrier and its resistance to rodent attack, additional resistance may be afforded by an effective chemical repellent. Such material should prevent or minimize damage by rodents upon paperboard, fabrics, or other materials impregnated, coated, or otherSince just before World War II increased importance has been placed on the use of chemical repellents for reducing damage by rodents, deer, rabbits, and other mammals that damage orchards, agricultural crops, and seed and seedlings in reforestation. Emphasis has been placed on repellents for commensal rats and mice to minimize damage to food packages, textiles, electrical wiring, and other materials in storage and transit. Approximately 4000 chemicals have been examined by a procedure involving food-acceptance tests, barrier tests, and simulated and actual field tests. Amines, nitro compounds, disulfides, and other classes containing nitrogen, sulfur, or halogens have been found repellent to the Norway rat, and efforts are being made to establish the most effective material and optimum methods for its application. Of compounds tested, actidione, an antibiotic, has been by far the most effective, but its toxicity, limited availability, and high cost make it useful only as a standard of comparison for other potential repellents. Complexes with trinitrobenzene, principally the aniline and o-anisidine derivatives, have been particularly effective. Other promising compounds include commercially available materials such as zinc dimethyldithiocarbamate-cyclohexylamine complex, thiuram disulfide, and hexachlorophene. Potentially, chemical repellents offer the chemical industry an outlet for many new products.

wise treated with the candidate chemical. The requirements for such a substance are rigid and may be summarized as follows:

It must have a low order of toxicity and be nonirritating, or capable of application in such a manner that its use does not involve hazards to personnel handling the finished product.

It must not have adverse effects upon bacteriostatic and fungistatic properties of the treated article, nor upon other desirable qualities such as strength, resiliency, or durability. It must be free of objectionable odors or

taste under the conditions of use.

It must be capable of application under conditions normally encountered in the fabrication of paperboard and other packaging materials.

must be sufficiently stable to ensure continued efficacy under varied conditions of handling, shipping, and storage. It must be available at a price that will

not unduly increase the cost of articles to be protected.

The studies conducted by the Fish and Wildlife Service under grants from the Office of the Quartermaster General have as their immediate objective the discovery of materials meeting these requirements, with specific reference to protection of packaging containers, plastics, electrical insulation, and similar materials.

The ultimate test of the efficacy of any material as a rodent repellent would involve measurement, or comparison, under field conditions, of the protection afforded cartons or other materials against rodent attacks. However, because such tests are difficult to perform and require considerable time and effort, it would not be feasible to examine large numbers of materials in this manner. As little or no information concerning the possible composition of potentially successful repellents was available at the start of these studies, it was necessary to devise an effective screening and testing program. As carried out by the Fish and Wildlife Service, this involved four distinct phases: (1) food-acceptance tests in which large numbers of samples are screened with a view to eliminating inactive substances and obtaining information on the possible correlation between chemical composition and repellent activity, (2) barrier tests to determine the efficacy of repellent materials when applied to test panels of paperboard, (3) exposure tests under carefully controlled conditions simulating those encountered in commercial warehouses to determine the degree of protection to test cartons, and (4) field tests to appraise the effectiveness of these materials when exposed to rodent populations under normal conditions. To facilitate this program initial screening of candidate compounds is carried out at the Services Patuxent Wildlife Research Laboratory, Laurel, Md. Materials found promising

are then sent to Denver for further evaluation. Techniques developed have been described in detail (1, 2, 6, 27) and are summarized here.

## Food-Acceptance Tests

In the initial or screening operation the candidate repellent is mixed with ground laboratory chow to form 2% of the total weight of the material. Individually caged laboratory rats are given two food cups, one containing 20 grams of this treated food and the other, 20 grams of similar untreated food. Food consumption is determined daily during a 4-day period and the repellent activity of the compound is expressed numerically according to the formula:

Repellency (K) = 
$$100 - \frac{1}{100w} \times (8T_1 + 4T_2 + 2T_3 + T_4) \times (U_1 + U_2 + 2U_3 + 4U_4 + 8X)$$

Table I. Time Required for Wild Rats to Penetrate Test Boxes Coated with Active Repellent Compounds<sup>a</sup>

Repellent Coating	Repellent Concn., G./Sq. Inch Box Surface	No. of Test Boxes	Av. No. of Days Until Penetrated by Rats
Untreated (control)		11	3.9
Z. A. C $b$ in starch paste	0.05	11	37.1
Trinitrobenzene in starch paste	0.05	11	38.2
Trinitrobenzene-o-anisidine complex <sup>c</sup> in starch paste	0.05	11	38.7
Trinitrobenzene-aniline complex <sup>c</sup> in starch paste	0.05	11	43.4
Actidione <sup>d</sup> in starch paste	0.03 and 0.01	4	Undamaged at 4 months
Actidione in starch paste	0.005	2	92
Actidione in starch paste	0.0025	2	22
General and the second se			

mulated warehouse tests. Boxes subjected to captive wild rats held under restricted <sup>b</sup> Supplied by B. F. Goodrich Chemical Co., Cleveland, Ohio.
 <sup>c</sup> Supplied by Edwal Laboratories, Inc., Ringwood, Ill.
 <sup>d</sup> Supplied by Upjohn Co., Kalamazoo, Mich.



Figure 1. Food-acceptance test Laboratory rat subjected to repellent-treated food (right) and untreated food (left)

where  $T_1 \ldots T_4$  represents the consumption (in grams) of the treated food on the respective days of the test,  $U_1 \ldots U_4$ represents the daily consumption of the untreated food, W is the body weight (in kilograms) of the test animals, and X represents the weight of untreated food remaining at the end of the test. The formula is based on the assumption that in the absence of repellent activity, all food should be eaten by the end of the third day, and that feeding pressures on treated food become more severe as the supply of untreated food is exhausted. Any residue of untreated food would indicate abnormalities in feeding, with the possibility that sublethal quantities of the test material had resulted in abnormal animals. If the repellency index is at least 85, the compound is rated as showing some significant degree of repellency and rescreened at levels of 2, 1, and 0.5%. If K values above 85 are obtained in all these tests, the compound is subjected to barrier testing.

## **Barrier Tests**

Although the food-acceptance tests furnish evidence that rats will refuse food containing certain materials, they do not establish that these materials will prevent rats from gnawing through treated paper. Nor do they offer a measure of effectiveness of materials which alter such physical characteristics as the resistance to tearing or the hardness, grittiness, or tackiness of the surface of the paper. Information on these points is obtained in the second phase of the test program.

Following a procedure similar to that used by Stolurow (16), laboratory rats selected at random as to sex and color have been used in these tests. Experimental cages have been specially equipped so that a test animal could be separated by a treated paper barrier from food which serves as the goal or driving urge. Since rats are not equally active in their tendency to gnaw, they must be subjected to an intensive training period extending over a period of weeks prior to use to ensure relative equivalence of performance both between animals and for animals in different tests. This has been accomplished by giving animals progressively more difficult barriers to penetrate to reach food until penetration of a standard barrier consisting of 10 sheets of 16-pound kraft paper laminated with synthetic latex or the equivalent is accomplished in repeated trials in 10 to 20 minutes.

Candidate chemical repellents may be added to the barrier by impregnation of one or more of the layers of the paper, by dusting on the surface coated with an adhesive, or by coating the barrier surface with a solution or suspension of the compound in a binder. Physical repellents may be added by coating one or all of the layers of paper comprising the barrier. The time required for penetration of these treated panels, as compared with penetration time for similar untreated panels, is taken as an index of the efficacy of the candidate material.

The barrier tests are much more complicated than the food-acceptance studies and introduce a number of new problems. First, it is difficult to obtain standardization of the rats to ensure uniformity of rate of attacks. Some rats never seem to learn that food can be obtained by gnawing through such barriers. All animals must be starved for 24 hours immediately prior to the test period to ensure proper motivation. Even with properly trained and motivated animals, it is difficult to obtain consistent working for more than 60 minutes, and it is necessary to replace the animals at the end of this period.

A second problem connected with these barrier tests consists of determining methods for application of the repellent. It has been impossible to obtain satisfactory results through impregnation of the paper, and the most effective method of application has involved formation of a surface coat containing the active material. Starch, lacquers, various plastics, and synthetic latices and resins have been used to hold the repellent upon the paper. Some adhesives apparently react with different repellents; nearly all adhesives appear partially to mask the repellent properties. For experimental purposes starch has been most widely used, as it seems to interfere less than other adhesives tested.

## **Exposure Station Tests**

The third and probably the most important step in evaluating candidate compounds consists of the exposure of treated articles to wild rodents under conditions resembling those encountered in normal storage. Test compounds are applied to the surface of  $8 \times 4 \times 8$  inch fiberboard cartons for appraisal. Starch paste has largely been employed in making these applications; however, lacquer, plastics, resins, and latices have also been used. Each station consists of a rodentproofstructure housing a colony of wild rodents maintained under near normal conditions. Ample harborage is provided, but food supplies are regulated to motivate attack upon the food-containing cartons. Five stations are maintained in Denver with auxiliary units located at Gainesville, Fla., and Laurel, Md.

Efficacy of the test treatment is determined by differential rates of attack upon treated and untreated cartons and comparisons made with known resistant materials.

## **Field Tests**

To supplement and bring to a logical conclusion the research being carried out in the laboratory, field trials are conducted with promising materials applied to fiberboard boxes, cloth bags, and other materials. Here again, the differential in penetration times for treated and untreated materials constitutes the measure of protection afforded by the test chemical.

In the search for repellents more than 4000 chemicals, chiefly organic compounds, have been screened by the foodacceptance technique. On the basis of these data, some of which have been reported (3), classes of chemical compounds, such as the carboxy acids, alcohols, amides, esters, ethers, and nitriles, give little or no indication of repellent activity. On the other hand, many fatty amines and their salts, guanidines and quaternary ammonium, pyridinium, nicotinium, and quinolinium salts have shown marked repellency under the test conditions. Most repellent compounds contain nitrogen, sulfur, or halogen. Although a very few insect repellents have shown repellency to rodents, a number of fungicides have shown considerable degrees of activity. It may be concluded, therefore, that fungistatic activity furnishes a rough index to repellency to rodents. Because of this observed correlation, it has become possible to eliminate many classes of compounds from consideration, and to concentrate upon more promising materials.

Approximately 20% of the compounds screened have been found sufficiently active for further testing, but demonstration of their utility in barrier control has not been without its difficulties. The problem is complicated by the fact that a rat may be able to gnaw through an obstruction such as a paper barrier or box without ingesting the excised particles, and by the fact that the efficacy of a repellent, when applied to paper, may vary according to the method of application and the concentration per unit area. Other factors, not fully understood, may also influence the results.

Evidence of this has been borne out in studies with several hundred candidate compounds found effective when mixed with food but which, when applied to barriers and test boxes, failed to prevent penetration for any considerable length of time. Experiments with the highly toxic compound, sodium fluoroacetate (1080), applied to barriers as an impregnate and as a surface coating in an adhesive served to verify this observation further. In tests conducted, individually caged laboratory rats gnawed through barriers containing this poison without ill effects, even though the quantity of paper removed contained enough of the lethal material to kill 15 animals if ingested. Further evidence of this ability of rats to gnaw through paper without ingesting appreciable amounts of a compound applied to it has been obtained in experiments conducted with dyes, pigments, and fluorescent compounds used as tracers.

In view of these findings, the results obtained in food-acceptance tests might be questioned as an index to the efficacy of the compounds when applied to papers. To determine this point, a series of experiments involving nearly 50 compounds and nearly 400 barriers was conducted (2). All compounds were applied at a concentration of 50 mg. per square inch to barriers composed of five sheets of kraft paper laminated with a synthetic latex. It was found that compounds giving a low repellency index (below 80) in the food-acceptance tests produced little change in the time required to pierce the barriers; that compounds having index values between 81 and 90 gave an average increase in time

Table II.	Acceptance of A	Actidione Solutions k	by Different Species of Rodents <sup>a</sup>
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Rodent	Actidione Solution, Mg./L.	Duration of Test, Days	Av. Ml. Taken per Animal per Day	Kill
Deer mice (Peromyscus)	Tap water (control) 10 100	14 14 13	$2.3 \\ 1.3 \\ 1.0$	0/10 0/10 3/10
Meadow mice (Microtus)	Tap water (control)	13	8.1	0/5
	10	13	5.3	3/5
House mice (Mus)	Tap water (control)	12	2.4	0/10
	10	12	0.79	0/10
	100	12	0.5	1/10
Harvest mice (Reithrodontomys)	Tap water (control)	13	1.84	0/10
	10	13	0.67	0/10
Laboratory rat <sup>b</sup>	Tap water (control) 10	11 11	16.8 Negligible	0/4

<sup>a</sup> Test animals provided either mixed grains or laboratory chow during studies.
 <sup>b</sup> Animals given small amounts of carrot starting on fourth day to provide some moisture.

until penetration; and values between 91 and 100 resulted in an additional increase in penetration time.

During these investigations over 400 compounds and formulations have been appraised for rodent resistance when applied to barriers and paper cartons. For the most part a thin starch paste was used in forming the surface coatings, although other adhesive materials have been tested.

In these studies one compound known as actidione, 3-[2-(3,5-dimethyl-2-oxocvclohexvl)-2-hydroxyethyl]glutarimide, an antibiotic, has been shown to stop all rodent attacks upon treated paperboard under both laboratory and simulated field conditions (18). As presented in Table I, this compound possesses about 20 times the repellent activity, on a weight basis, shown by other

Figure 2. Equipment for evaluating rodent resistance of repellent-treated paper barriers



promising compounds. It also exhibits definite species variation. Laboratory rats refused to drink solutions containing as little as 10 mg. per liter of this compound, while house mice, deer mice, harvest mice, and meadow mice drank appreciable amounts based on comparisons made with controls of tap water over an extended period. Evidence of the species variation in acceptance of this material is given in Table II. The toxicity, limited availability, and present high cost of this compound, however, make it useful only as a standard of comparison for other potential repellents. In current experiments, fiberboard boxes containing 2 to 3 mg. of actidione per square inch, applied as a surface coating, are being used for this purpose.

Two other highly effective compounds were developed in the service's laboratories. Early studies had shown that many amines were repellent and that the activity was enhanced through the presence of nitro groups. A series of some 20 amine complexes with trinitrobenzene was prepared; the aniline and o-anisidine derivatives were particularly effective (7).

Other promising compounds include commercially available materials such as zinc dimethyldithiocarbamate-cyclohexylamine complex (Z.A.C.), tetramethylthiuram disulfide, and hexachlorophene.

Tests of commercially prepared samples of cartons treated with these and other compounds have shown that increased protection may be obtained through their use (26). The cartons were prepared by roll-coating paperboard with Hycar latex and vinyl films, containing the repellent, so that a final concentration of about 8 to 10 pounds of the chemical per 1000 square feet was produced. Table III gives the results obtained in a series of 19 tests, in which the boxes were subjected to the combined attack of wild Norway and roof rats

VOL. 2, NO. 3, FEBRUARY 3, 1954 145 under simulated warehouse conditions.

As shown, the two trinitrobenzene complexes, zinc dimethyldithiocarbamate-cyclohexylamine complex, tetramethylthiuram disulfide, and hexachlorophene were the most active of the test compounds in affording protection against rodent damage. Unfortunately, all of these repellent compounds are not compatible with both types of film and, except in the case of zinc dimethyldithiocarbamate-cyclohexylamine complex, a comparison of the effectiveness of the same repellent in both films was not possible. From the results obtained with this compound it would appear that less interference occurred when the repellent was employed in latex film than in vinyl.

Under storage conditions a number of repellent compounds bloom or sweat out. The influence of this migratory property on the activity of a compound in an impervious film is not known, but indica-tions are that it is beneficial. The chemical being held loosely on the surface of a film allows for the direct contact of the compound with the mouth parts of an attacking animal. Compounds showing the greatest rodent repellency in these tests were those that have a tendency to migrate.

Field tests with these commercially prepared cartons indicate that all treatments possess some protective properties. Exposed for over a year now, these boxes have resisted Norway rat penetration. Considerable stripping of the film has

occurred on boxes where the poorer repellents were employed and on those bearing untreated vinyl and Hycar films. Except for untreated boxes, none has been penetrated by rats.

Further evidence of the resistance to rodents of the trinitrobenzene complexes and zinc dimethyldithiocarbamate-cyclohexylamine complex has been obtained in a series of tests in which these repellents were incorporated in a 5-mil vinyl film, at concentrations ranging from 25 to 45 mg. per square inch (28). These films were applied to cartons as loose wraps and successfully resisted rodent attacks for several months under conditions where untreated films were destroved within 2 weeks.

In recent field tests burlap bags treated with these compounds have also shown appreciable protective properties. In these tests trinitrobenzene-aniline complex applied at a concentration of 11 mg. per square inch afforded most resistance to rat attack. Zinc dimethyldithiocarbamate-cyclohexylamine complex, at somewhat higher concentration (16 mg. per square inch), was less resistant but also showed good results. Both treatments exhibited significant protection when compared to commercially available repellent-treated bags and to untreated bags (see Table IV).

The results of this test and others reported herein are felt to be significant, since efforts have been made in each case to produce optimum conditions

#### Table III. **Relative Resistance of Commercially Prepared Coated Boxes** to Rodent Attack<sup>a</sup>

(Evaluation carried out under simulated warehouse conditions)

•			,	
Treatment	Dry Weight of Repellent, Lb./1000 Sq. Feet	No. of Series Tested	Percentile Score (Norway ond Roof Rats Combined)	Rank
Trinitrobenzene-aniline complex <sup>b</sup> in Hycar				
latex film	83	19	70.4	1
Z.A.C. <sup>c</sup> in Hycar latex film	6.7	19	67 0	2
Trinitrobenzene-o-anisidine complex <sup>b</sup> in	0.17		07.0	-
Hycar latex film	8.1	19	64.6	3
Tetramethylthiuram disulfide <sup>b</sup> in vinyl film	10.3	19	62.2	4
Hexachlorophene <sup>e</sup> in vinyl film	10.4	19	61.1	5
Z.A.C. in vinyl film	7.7	19	56.9	6
Blank vinyl film		19	56.6	7
Rosin amine D-acetate <sup>f</sup> in vinyl film	9.3	19	53.2	8
Tetramethylthiuram monosulfide <sup>d</sup> in vinyl				
film	9.3	19	51.2	9
$\beta$ -Isothioureidopropionic acid <sup>e</sup> in Hycar				
latex film	7.6	19	48,3	10
Blank Hycar latex film		19	46.8	11
Rosin amine $D^{f}$ in vinyl film	7.3	19	45.1	12
Sodium silicofluoride <sup>9</sup> in Hycar latex film	8.9	6	43.7	13
Sodium silicofluoride in vinyl film	17.1	19	35.9	14
Sodium silicofluoride in Hycar latex film	9.3	19	35.2	15
Rosin amine D-pentachlorophenate <sup>f</sup> in				
Hycar latex film	7.7	19	30.6	16
Untreated	• •	14	23,4	17
		-		

<sup>a</sup> Test V3-S boxes prepared by Paulsboro Manufacturing Co., Philadelphia, Pa. <sup>b</sup> Chemicals obtained from Edwal Laboratories, Inc.

<sup>c</sup> Chemicals obtained from B. F. Goodrich Chemical Co. <sup>d</sup> Chemicals obtained from Naugatuck Chemical.

<sup>g</sup> Chemical obtained from Blockson Chemical Co.

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for rodent attack. Under less exacting conditions greater protection may be expected.

## **Application Methods** (For Rodent Repellents)

One of the basic problems in the study has been the development of procedures for application of repellents. Three possible methods have been considered for application to paperboard: impregnation of the fibers, either in the beater or through addition in volatile solvents to the finished product; addition in the glue lines; and surface coating in suitable carriers. For initial test purposes a surface concentration of from 30 to 50 mg. of the repellent per square inch was applied, although a lower concentration would be necessary for commercial production.

As summarized by James B. DeWitt of this service, impregnation of the fibers has been found impractical. Addition in the beaters would involve considerable waste of the repellent compound and result in inferior papers. In fact, impregnation at any stage seems to result in nonreversible adsorption of the repellent, with little or no activity.

Glue-line application has also met with little success. Bonding properties are decreased and the paperboard is weakened. In addition, little repellent effect is produced and it is assumed that activity is masked by the adhesive or lost as a result of burial in the paper plies.

Application as a surface coat appears to be the most effective procedure. In laboratory application, starch, lacquers, chlorinated hydrocarbons, plastics, waxes, and latex formulations have been used as carriers. Starch has appeared to give the greatest activity of the repellent. It is assumed that repellent particles are occluded by some of the other carriers. Some repellents are incompatible with certain carriers, and it has been necessary to vary procedures accordingly.

Several lots of paperboard and cartons have been prepared commercially using wax formulations as carriers. No repellent activity was apparent with materials applied in waxes, and it was apparent that the technique of application was faulty, or that the wax completely masked the repellent effects. It is possible that changed techniques might show that wax application could be employed. Inasmuch as many paper companies use wax-coating machines in normal manufacturing practice, it would be advantageous to adopt the repellent treatment to existing practices.

In other studies, cartons have been prepared commercially by roll-coating paperboard with latex and vinyl films containing 8 to 10 pounds of the repellent per 1000 square feet. Such films have been more satisfactory than waxes, but

Chemical obtained from Sindar Corp. Chemicals obtained from Hercules Powder Co.



Figure 3. Evaluation of rodent resistance of test carbons and other materials under exposure station conditions

several difficulties have been encountered. Many of the more active repellents coagulate the latex on contact and make it impossible to secure satisfactory films. Heavy loading also weakens the film, or reduces its adhesion to the paperboard. Despite these difficulties, the greatest protection obtained with commercially prepared materials has been through the addition of repellents to these films.

The development of satisfactory methods for application of repellents is one of the most pressing problems at this time. On the basis of comparison between commercially prepared materials and those prepared in the laboratory, it is obvious that much of the repellent activity has been lost or masked in the normal commercial procedure. To overcome these difficulties, the following have been suggested:

The use of other film formers such as Aroclors [resinous products (chlorinated biphenyl and chlorinated polyphenyls), Monsanto Chemical Co.], cellulose acetate, and cellulose nitrate. Experiments have shown that combinations of Aroclors with trinitrobenzene complexes produce effective rodent-repellent films. Volatile solvents which are objectionable in packaging manufacture might be minimized by the preparation of water-emulsifiable concentrates.

The fortification of starch-repellent formulations with resins, latex, or other materials to improve water resistance and abrasion deterioration. Applications of this type should be useful in the preparation of textile materials.

Some of the difficulties with vinyl film have involved unsatisfactory bonding to the paperboard. Two possible solutions have been offered. In one, the board could be given a 3- or 4-mil coat of untreated vinyl, and this coated board be passed through roll coaters to give an additional 5-mil film containing the repellent. The other suggests that board treated with a 5- to 7-mil film be heated until the film softens, then the repellent be pressed into this softened film. Although these suggested methods of repellent application have been presented with the preparation of paper and paperboard products in mind, their use in the development of rodent-resistant textile products, cordage, electrical insulation, industrial tapes, adhesives, plastic tubing, and other materials vulnerable to rat attack is also a possibility. Work on some of these has been reported (20, 22). Others are currently being investigated by this service.

In the packaging field, animal foods alone are estimated to require 400,000,-000 bags annually. This and the uses just mentioned indicate the potentialities of this field of research to the chemical industry. This does not consider the vast number of containers employed in packaging food and other materials for human consumption.

To perfect useful and practical materials for this purpose the combined efforts of the testing agency, synthetic chemists, paper and plastic technologists, servicemen dealing with coating and preservation of paper and other products, as well as rodent-control specialists will be needed.

Certain readily available compounds such as sodium silicofluoride, lye, creosote, and lime-sulfur are sometimes used in the burrows and runways of rats to discourage activity. In warehouses and similar structures where sacked seed grain is stored, a liberal application of powdered sulfur or flake naphthalene scattered over the bags has been found beneficial in reducing rat attacks (14). Finely powdered ammonium sulfate intimately mixed in approximately a 20% concentration with cellulosic insulation material such as ground paper, cotton, or sawdust has been found useful in minimizing rodent nesting. Nicotine sulfate, coal tar, oil of citronella, and a variety of other substances have also been mentioned as objectionable to rats (12). The use of these materials is limited, however, and does not constitute any appreciable market for these products.

## **Repellents for Field Mammals**

Damage by field rodents and other native wildlife, though of less magnitude, is nevertheless of considerable economic importance. The principal offenders are rabbits, field mice, tree squirrels, porcupines, and deer-creatures that feed on agricultural crops, seed and seedlings in reforestation projects, shelterbelt plantings, and orchards. Tree squirrels also inflict considerable losses on the lead sheaths of overhead telephone cables, while pocket gophers attack underground cables in much the same manner. Losses in excess of \$100,000 a year have been reported as a result of damage of this type alone. Countrywide, the damage done by field animal pests amounts to many millions of dollars. As in rat control, the application of repellents to solve these problems has limitations. Where reduction in animal populations may be prohibited by law, as in the case of deer and cottontail rabbits, or where poisoning is impractical, repellents have been found useful. The application of chemical repellents directly on trees, gardens, and other agricultural crops has met with considerable success. This, in part, may be due to the fact that the spray or paint becomes a part of that portion of the plant actually ingested by the animals. This is not the case with packaging. Odor repellents and substances applied to rags or other materials and exposed as area repellents have not been particularly successful.

Thompson (17) has made a comprehensive study of the literature pertaining to repellents for preventing field mammal damage and has summarized the work in over 100 references examined.

## Rabbit and Deer As early as 1932,

the Fish and Wildlife Service undertook research in the reduction of damage by field mammals through chemical repellents. During this period a rabbit repellent known as. 96A which contains lime-sulfur and copper salts as the active ingredients was developed (8, 25). When applied to the bark of dormant trees and coniferous seedlings, this material is effective in preventing damage by rabbits and of value in minimizing field mouse damage. More recent studies have demonstrated the value of such compounds as zinc dimethyldithiocarbamate - cyclohexylamine complex, tetramethylthiuram monosulfide, tetramethylthiuram disulfide, and trinitrobenzene-aniline complex as repellents for these creatures (4). In controlled tests carried out this

past winter, spray and paint formulations containing these compounds with polyethylene polysulfide, Hycar latex, or Aroclors as adhesives, effectively protected Chinese elm and apple trees against rabbit damage throughout the dormant season. Repellent 96A, a rosin-alcohol formulation (5), and a number of commercial materials tested were less effective. This work revealed also that the ratio of adhesive to the repellent is important, since to be effective a repellent film must remain on the tree for approximately 6 months. Failures reported with commercially available repellent materials may be largely due to poor adhesion of the protective film. Ratios of 1 part of adhesive to 2 parts of repellent seem most desirable. Aside from their repellent activity, the advantages of these materials over most of the existing repellent preparations are that they may be prepared in waterdispersible formulations and applied as sprays rather than paints, thereby reducing costs and facilitating applications to trees or agricultural crops. As with any pesticide, consideration must be given to the phytotoxic effects of the compounds when applied to plants. No ill effects were observed when these materials were applied to the trunk of trees in concentrations as high as 20%. In field practice, concentrations considerably lower than this would be used. A number of sprays and dusts have been developed for application to truck and garden crops (9, 10). One of the most recent of these is a proprietary product containing zinc dimethyldithiocarbamate-cyclohexylamine complex (24).

Deer, like rabbits, damage forest plantations, young orchard trees, and garden crops. Although a large number of materials have been tested (23),  
 Table IV.
 Resistance of Repellent-Treated Burlap Bags to a High Population of Norway Rats Under Field Conditions

Treatment	Repellent Concn., Mg./Sq. Inch	No. of Bags Exposed	No. of Days Until Bags Penetrated by Rats		
			Min.	Max.	Av.
Trinitrobenzene-aniline complex in Aroclors	11	15	32	46	40.8
Z.A.C. in polyethylene polysulfide	16	15	9	42	33.6
Commercial bag A	Unknown	15	4	32	23.1
Commercial bag B	Unknown	15	1	18	11.0
Commercial bag C	Unknown	15	1	16	5.9
Untreated (control)		15	1	9	4.7

zinc dimethyldithiocarbamate – cyclohexylamine complex and a proprietary spray containing anthracene have been the only repellent compounds widely used in this country. In general, materials useful in rabbit control are also of value as deer repellents.

Mice and Other Small Mammals Forest rodents, particularly whitefooted mice (*Pero*-

myscus), cause considerable damage to forest seeds, and they often are the limiting factor in the regeneration of forest stands by direct seeding. Early efforts to prevent this damage through the use of repellents met with little success. In the Fish and Wildlife Services Laboratory at Denver, nearly 100 compounds were tested. Application was made by coating the seeds and by incorporating the deterrent material in a matrix employed in pelleting seeds (13). The removal of the hull which carries the repellent coating by the mice when feeding appears to contribute to the ineffectiveness of the method. There is danger also of inhibiting germination by pelleting the seed. In recent work, Spencer and Kverno (15) have found that by soaking the seed in solutions containing the re-

Figure 4. Repellent-treated burlap bags exposed to wild rat populations under field conditions

Note damage done to poorer treatments and untreated bags



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pellent, better results are obtained. As there is danger of reducing viability by this method, not only feeding tests but germination tests must be carried out to evaluate each seed treatment.

One compound holds particular promise. This is tetramethylene disulfotetramine, which has been given the name "tetramine" for brevity. Seeds soaked in an acetone solution containing 1% of this chemical are avoided by mice and in field tests have produced satisfactory stands of forest seedlings, while almost all untreated seeds were consumed. The chemical is not a true re-pellent, in that a number of seeds are sacrificed in educating the animals against it; being a highly toxic compound, some animals are killed. In laboratory and field tests, however, it has been found that by far the greater number of rodents become sensitized following initial contact with treated seed and thereafter avoid them. Studies have revealed, also, that seedlings grown from tetramine-treated seed are protected against mouse feeding for several weeks after germination.

Although damage to trees and agricultural crops by field mice and other small rodents assumes considerable proportions at times, limited use has been made of repellents as a control measure. Meadow mice (Microtus) and other burrowing rodents damage trees and other crops under cover of mulch or below the soil level, where the application of repellents is not practical. Studies carried out with planted seed corn indicate that relatively high concentrations of repellent are needed to provide protection against rodent attack (29). Soil adsorption, leaching, and other processes apparently reduce the effectiveness of the material. Experimentally tetramethylthiuram disulfide, when dusted on seed corn in storage, in a concentration of 2 ounces per bushel, proved to be effective as a repellent for house mice.

Though porcupines normally stay close to forested areas where they feed on the bark of trees and other plant materials, they are at times attracted to human habitations, where they may damage buildings, equipment of various kinds, and agricultural crops. Because

of their strong desire for salt, they often are very destructive to handles of tools, outdoor facilities in recreational areas, and other accessible wooden structures that are heavily used by humans. To combat destruction of the latter type, copper naphthenate has been found most satisfactory. Ammonium thiocyanate solution and pentachlorophenol in a penetrating oil have also given promise. Zinc dimethyldithiocarbamate-cyclohexylamine complex, though not extensively used, has been employed in minimizing damage to orchard trees and agricultural crops.

Damage by tree squirrels and pocket gophers to communication cables is of considerable importance. Much work has been carried out in attempting to determine the reasons for these attacks and in devising methods of control (11, 21, 30). Where appraised, chemical repellents have shown little promise. Protection by mechanical devices, such as a stainless steel tape wrap, hardware cloth, or a paint containing ground glass or sand, though not entirely satisfactory, has proved more effective.

A new and little investigated field for chemical repellents is their application to soil to discourage burrowing animals such as pocket gophers, moles, and mice. There is some evidence that these animals avoid soil contaminated with compounds such as benzene hexachloride. Similar observations have been made where tung nut pumice was applied to the soil as a fertilizer. In recent studies, repellent materials introduced into the soil of ditch banks as protection against pocket gopher damage have been found to have possibilities (19). The vertical seam of repellent-treated earth serves as a barrier through which the animals are reluctant to burrow. Even herbicides may influence certain rodent populations through the removal of forbs and fleshy plants, often principal food sources.

Rodents like other creatures are quick to adapt themselves to changing conditions, particularly if survival is at stake. The protection afforded packaged food and agricultural crops by a repellent, therefore, is dependent largely on the availability of other sources of food. Where this is scarce, and reductional control is impossible or impractical, protection of materials of economic importance with repellents is difficult and failure may result. Under normal conditions, however, it is believed substantial protection can be maintained. Potentially, chemical repellents offer the chemical industry an outlet for many new products.

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Figure 5. Untreated apple tree (left) damaged by cottontail rabbits. Repellent-treated tree (right) is undamaged

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