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## UREA-FORMALDEHYDE RESIN AS A VEHICLE FOR SEMI-PERMANENT INSECTICIDAL RESIDUES TO CONTROL FLIES AND MOSQUITOES

**Riassunto.** — Una delle questioni di attualità nella tecnica degli insetticidi a effetto rimanente è la messa a punto di veicoli stabili, capaci di mantenere l'insetticida nella sua massima attività durante diversi mesi. Le pitture, verniciature e resine sintetiche miste ad insetticidi sono state sperimentate in questi ultimi anni come rivestimento al legno, al metallo e ad altri materiali.

Il presente lavoro espone le ricerche effettuate con una resina all'urea formaldeide, usata come veicolo d'insetticidi tossici per le mosche e le zanzare. Si è cercato, stabilendo diverse formule, di combinare le qualità insetticide con le qualità protettive, in modo che i rivestimenti possano essere fabbricati industrialmente ed entrino nell'uso corrente.

Una efflorescenza cristallina appare dopo un tempo più o meno lungo alla superficie di certe vernici o resine con aggiunta di DDT o di altri insetticidi solidi. Questa efflorescenza, che risulta da una migrazione del DDT verso la superficie, avviene spontaneamente o in seguito all'attività degli insetti sulla superficie del rivestimento. L'efflorescenza eliminata asciugando e lavando, riappare spontaneamente su alcuni rivestimenti. La sovrasaturazione della preparazione di DDT non è sufficiente a rendere conto di questo fenomeno che rimane inspiegato. La tossicità del rivestimento dipende da questa efflorescenza.

Dopo aver esaminato diversi tipi di vernici, lacche e resine, la durata e il grado della loro tossicità, la quantità d'insetticidi optima da aggiungerci. L'A. si ferma particolarmente sulle resine a base di urea-formaldeide che danno i risultati migliori.

I metodi di saggio della tossicità dei rivestimenti — esponendo alle pareti ricoperte di queste lacche insetti in gabbie o placche di Petri e determinando il tasso di mortalità — sono molto diversi e i risultati

ottenuti da differenti autori sono difficilmente paragonabili. La resina utilizzata dall'A. per i suoi esperimenti ha la seguente formula:

|                                                      |      |               |
|------------------------------------------------------|------|---------------|
| Resina all'urea-formaldeide BE610 . . . . .          | 50   | parti in peso |
| Resina agli alcali di olio di ricino BA502 . . . . . | 50   | parti in peso |
| Butanolo . . . . .                                   | 27,5 | parti in peso |
| Xilolo . . . . .                                     | 27,5 | parti in peso |
| Insetticida . . . . .                                | 12   | parti in peso |

Il tenore della preparazione insetticida è di 20% del peso del contenuto solido. E' indurita con gli acidi o il caldo o con i due metodi combinati. I principali insetti utilizzati, *Musca domestica* e *Aedes aegypti*, rappresentavano il primo degli insetti che si spostano con la marcia e col volo, il secondo gli insetti essenzialmente volanti.

L'essiccamento e l'indurimento delle lacche è stato studiato rispetto alle loro proprietà insetticide. Le lacche più dure si sono rivelate meno tossiche per via di una minore efflorescenza cristallina alla superficie. La tossicità delle lacche per *Aedes* è cresciuta con la loro duttilità. La tossicità delle lacche molto dure non era aumentata dopo due mesi. L'A. espone i risultati ottenuti con diversi rivestimenti contenenti quantità variabili di « materia per indurire » e di « materia per rendere plastico ». (E' il caso di tenere conto nel valutare la durata dell'attività rimanente delle perdite in DDT con l'eliminazione della fluorescenza quando si lava o si asciuga la superficie). Studia inoltre l'azione dei raggi UV utilizzati qualche volta per l'indurimento. Gli UV diminuiscono l'efflorescenza e quindi la tossicità, ma la loro azione è solo superficiale. Non riducono, come nel caso delle soluzioni idrocarburate, la tossicità del DDT stesso. L'uso di solventi a punto di ebollizione elevato è consigliabile per evitare un indurimento troppo forte.

L'esperienza ha mostrato che l'efflorescenza non si produce nei rivestimenti contenenti meno del 5% di DDT e altri insetticidi sono stati messi alla prova. Una serie di formule di lacche per azione rimanente prolungata, contenenti piretro, è stata messa al punto nella speranza che siano attive contro i ceppi resistenti al DDT come alcuni ceppi di mosche della Sardegna. I risultati non sono stati molto incoraggianti. Ma d'altra parte ci si è accorti che l'aggiunta al piretro di altre sostanze, quali l'BHC e il butossido di piperonile rinforzava la sua tossicità, in particolare rispetto ai ceppi resistenti al DDT. In un modo generale ci si è potuto rendere conto che gli insetticidi volatili avevano proprietà interessanti poichè contrariamente agli insetticidi solidi, la loro tossicità era massima nei rivestimenti di fresca preparazione e diminuiva con il tempo. Pensando che la presenza di nuove

molecole poteva influire sulla tossicità di questi insetticidi volatili, si sono preparati miscugli contenenti aldrine (2%), BHC (2%), acido «C», dieldrina e DDT. Una specie di sinergia si esercita fra queste diverse sostanze, le tre ultime aumentando la tossicità apparente delle due prime.

L'A. espone le differenze di tossicità di questi prodotti, secondo la natura della superficie sulla quale vengono applicati. Sottolinea la tossicità specifica di questi miscugli per certi gruppi di insetti. Discute il valore insettifugo dei rivestimenti e i servizi che il piretro, anche se costoso, può rendere nel confezionare queste preparazioni.

Accennando alla questione dell'applicazione pratica e alla collaborazione tra fabbricanti di lacche e fabbricanti di insetticidi, l'A. informa che già certe carte da parato per le abitazioni e certe carte da imballaggio sono state ricoperte di lacche insetticide. Esperimenti precisi sono stati fatti nelle cucine e nei magazzini delle navi ove mosche, blatte e tonchi sono stati eliminati in pochi giorni in presenza di rivestimenti insetticidi. Sembra probabile che questi ultimi potranno essere impiegati oramai nei locali e sulle superfici ove gli insetti riposano preferibilmente.

L'industria potrà offrire rivestimenti che rimarranno attivi per mesi, forse per anni, malgrado i frequenti lavaggi. Nei posti ben ventilati, i pericoli di intossicazione dell'uomo sono minimi. Questo procedimento di lotta appare economico solo per usi di lunga durata, di nove mesi almeno. Altri procedimenti come quello dell'impregnazione di striscie di carta sospesi poi lungo le pareti, possono essere poi preferiti in certi casi. I rivestimenti con resine insetticide applicate su reti metalliche o in fondo alle vasche d'acqua potrebbero avere una parte larvicida nella lotta contro le zanzare mantenendo un certo tenore in insetticidi nei piccoli raduni di acque stagnanti. Si può anche prospettare l'uso di rivestimenti nei fabbricati che hanno il vantaggio di evitare polverizzazioni o spruzzamenti ripetuti e di rendere il potere insetticida indipendente dal tipo di superficie.

L'A. indica il prezzo approssimativo di questi preparati, prezzo che non è facile paragonare esattamente con quello degli spruzzamenti secondo i metodi facili e che dipende da diversi fattori. I rivestimenti con resine insetticide avrebbero il vantaggio di sopprimere gli spruzzamenti e conseguentemente tutti i fattori di variazione che accompagnano l'applicazione attuale del trattamento con insetticidi ad azione rimanente.

**Résumé.** — Une des questions d'actualité dans la technique des insecticides à effet rémanent est la mise au point de véhicules stables,

capables de maintenir l'insecticide à son maximum d'activité durant plusieurs mois. Les peintures, vernis et résines synthétiques additionnés d'insecticides ont été mis à l'essai au cours des dernières années, comme revêtement du bois, du métal ou d'autres matériaux.

La présente étude expose les recherches effectuées avec une résine à l'urée-formaldéhyde, employée comme véhicule d'insecticides toxiques pour les mouches et les moustiques. On a cherché, en établissant diverses formules, à combiner les qualités insecticides avec les qualités protectrices, de façon que ces revêtements puissent être fabriqués industriellement et entrent dans l'usage courant.

Une efflorescence cristalline apparaît au bout d'un temps plus ou moins long à la surface de certains vernis ou résines additionnés de DDT ou d'autres insecticides solides. Cette efflorescence, résultat d'une migration du DDT vers la surface, se produit spontanément ou à la suite de l'activité des insectes sur les surfaces de revêtement. L'efflorescence, éliminée par essuyage ou lavage, reparaît spontanément sur certains revêtements. La sursaturation de la préparation en DDT ne suffit pas à rendre compte de ce phénomène, qui reste inexpliqué. La toxicité du revêtement dépend de cette efflorescence.

Après avoir passé en revue divers types de vernis, laques et résines, la durée et le degré de leur toxicité, les quantités optimums d'insecticides à ajouter, l'auteur s'arrête particulièrement aux résines à base d'urée-formaldéhyde, qui ont donné les résultats les plus favorables.

Les méthodes d'essais de toxicité des revêtements — par exposition d'insectes dans des cages ou plaques de Pétri aux parois enduites de ces laques, et détermination du taux de mortalité — sont très diverses et les résultats obtenus par divers auteurs difficilement comparables. La résine utilisée par l'auteur pour les essais a la formule suivante :

|                                                    |      |                  |
|----------------------------------------------------|------|------------------|
| Résine à l'urée-formaldéhyde BE640 . . . . .       | 50   | parties en poids |
| Résine aux alkyls d'huile de ricin BA502 . . . . . | 50   | parties en poids |
| Butanol . . . . .                                  | 27,5 | parties en poids |
| Xylol . . . . .                                    | 27,5 | parties en poids |
| Insecticide . . . . .                              | 12   | parties en poids |

La teneur de la préparation en insecticide est de 20% du poids du contenu solide. Elle est durcie par les acides ou la chaleur ou par les deux méthodes combinées.

Les principaux insectes utilisés, *Musca domestica* et *Aedes aegypti* représentaient, le premier les insectes qui se déplacent par la marche et le vol, le second les insectes essentiellement volants.



Le séchage et le durcissement des laques a été étudié, en rapport avec leurs propriétés insecticides. Les laques les plus dures se sont révélées les moins toxiques, par suite d'une moindre efflorescence cristalline à leur surface. La toxicité des laques pour *Aedes* s'accrut avec leur ductilité. La toxicité des laques très dures n'avait pas augmenté au bout de deux mois. L'auteur donne les résultats obtenus avec divers revêtements contenant des quantités variables de « durcissant » ou de « plastifiant ». (Il y a lieu de tenir compte, dans l'estimation de la durée de l'activité rémanente, des pertes en DDT par élimination de l'efflorescence, lors de l'essuyage ou du lavage). Il étudie ensuite l'action des rayons UV utilisés parfois pour le durcissement. Les UV diminuent la formation de l'efflorescence, donc la toxicité, mais leur action n'est que superficielle. Ils ne réduisent pas la toxicité du DDT lui-même, comme c'est le cas dans les solutions hydrocarburées. L'emploi de solvants à point d'ébullition élevé est à conseiller pour éviter un durcissement trop prononcé.

L'expérience ayant montré que l'efflorescence ne se produit pas dans des revêtements contenant moins de 5% de DDT, d'autres insecticides ont été mis à l'essai. Une série de formules de laques pour action rémanente prolongée, contenant du pyrèthre, a été mise au point, dans l'espoir qu'elles seraient actives contre les souches résistantes au DDT, telles que certaines souches de mouches de Sardaigne. Les résultats n'ont pas été très encourageants. Mais, on s'est aperçu par contre, que l'adjonction au pyrèthre d'autres substances, telles que le BHC et le butoxyde de pipéronyl, renforçaient sa toxicité, en particulier vis-à-vis des souches résistantes au DDT. D'une façon générale, on s'est rendu compte que les insecticides volatils avaient des propriétés intéressantes, que, contrairement aux insecticides solides, leur toxicité était maximum dans les revêtements fraîchement préparés, et qu'elle diminuait avec le temps. Dans l'idée que la présence de grosses molécules pourrait influencer sur la toxicité des insecticides volatils, on a préparé des mélanges contenant de l'aldrine (2%), du BHC (2%), de l'acide « C », de la dieldrine et du DDT. Une sorte de synergisme s'exerce entre ces diverses substances, les trois dernières augmentant la toxicité apparente des deux premières.

L'auteur mentionne les différences de toxicité des produits, suivant la nature de la surface sur laquelle ils sont appliqués. Il souligne la toxicité spécifique de certains mélanges pour certains groupes d'insectes. Il discute la valeur insectifuge des revêtements et les services que le pyrèthre, bien que coûteux, peut rendre dans ces préparations.

Abordant la question des applications pratiques et de la collabo-

ration entre fabricants de laques et fabricants d'insecticides, l'auteur mentionne que, déjà, des papiers peints pour les habitations et du papier d'emballage ont été recouverts de laques insecticides. Des expériences précises ont été faites dans les cuisines et les magasins des bateaux, où mouches, cafards et charançons ont été éliminés au bout de quelques jours par la présence de revêtements insecticides. Il semble probable que ces derniers pourront être employés désormais dans les locaux et sur les surfaces où les insectes se posent de préférence. L'industrie pourra offrir des revêtements qui resteront actifs des mois, voire des années, malgré de fréquents lavages. Dans les endroits bien ventilés, les dangers d'intoxication de l'homme sont minimales. Ce procédé de lutte ne paraît économique que pour des usages de longue durée, de 9 mois au moins. D'autres procédés, tels que l'imprégnation de bandes de papier qui seraient suspendues le long des parois, peuvent être préférés, dans certains cas. Les revêtements de résines insecticides appliqués à des treillis métalliques ou au fond de pièces d'eau pourraient jouer un rôle de larvicides dans la lutte contre les moustiques, en maintenant une certaine teneur en insecticide dans les petites collections d'eau. On peut envisager aussi l'emploi de revêtements préfabriqués, qui ont l'avantage d'éviter des pulvérisations répétées et de rendre le pouvoir insecticide indépendant du type de surface.

L'auteur indique le prix approximatif de certaines de ces préparations, qu'il n'est guère possible de comparer exactement avec celui des pulvérisations selon les méthodes classiques, qui dépend de plusieurs facteurs. Les revêtements de résines insecticides auraient l'avantage de supprimer les pulvérisations et par conséquent tous les facteurs de variation qui accompagnent l'application actuelle de traitement aux insecticides à action rémanente.

**Summary.** — One of the current problems in insecticide technique which still awaits solution is that of finding stable vehicles, capable of maintaining the insecticide at its maximum activity for several months. Paints, varnishes and synthetic resins have been experimented with in recent years as coatings for wood, metal and other materials.

The present study describes research carried out on a urea-formaldehyde resin, used as a vehicle for insecticides toxic to flies and mosquitoes. An attempt was made, by establishing different formulae, to combine insecticidal with protective properties, so that the coats could be made industrially and brought into everyday use.

A crystalline bloom appears after a more or less lengthy period on the surface of certain varnishes and resins when DDT or other solid

insecticides are added. This bloom, which results from a spreading of DDT towards the surface, appears spontaneously or following activity of insects on the surface of the coat. When the bloom is removed by wiping it away and drying the surface, it reappears spontaneously on some coats. Super-saturation of the DDT preparation is not enough to account for this phenomenon, which is still unexplained. The toxicity of the coat depends on this bloom.

After having examined various types of varnish, lacquer and resin, the duration and degree of their toxicity, and the optimum amount of insecticide to be added, the author concentrates particularly on resins with a urea-formaldehyde base: these give the best results.

The methods of testing the toxicity of the coats — exposing insects in cages or Petri dishes to walls covered with these lacquers, and determining the mortality rate — vary considerably, and results obtained by different authors are scarcely comparable. The resin utilized by the author for his experiments had the following formula:

|                                         |      |                 |
|-----------------------------------------|------|-----------------|
| Urea-formaldehyde resin BE610 . . . . . | 50   | parts by weight |
| Castor oil alkali resin BA502 . . . . . | 50   | parts by weight |
| Butanol . . . . .                       | 27.5 | parts by weight |
| Xylol . . . . .                         | 27.5 | parts by weight |
| Insecticide . . . . .                   | 12   | parts by weight |

The proportion of insecticidal preparation is 20% of the solid content. It is hardened by acids and by heat, or by both methods combined. The principal insects utilized, *Musca domestica* and *Aedes aegypti*, are representative respectively of insects which move both by crawling and flying, and of essentially flying insects.

The drying and hardening of the lacquers has been studied with respect to their insecticidal properties. The harder lacquers were less toxic, as shown by less crystalline bloom on the surface. The toxicity of lacquers for *Aedes* increased with their plasticity. The toxicity of very hard lacquers was not increased after two months. The author describes the results obtained with various coatings containing variable amounts of « hardening material » and of « material to increase plasticity ». (In evaluating the duration of long-lasting activity, one has to take into account the wastage of DDT caused by removal of bloom when the surface is wiped or washed). The action of the ultra-violet rays utilized several times for hardening purposes was also studied. Ultra-violet rays diminish bloom and thus toxicity, but their action is solely superficial. They do not reduce the toxicity of DDT itself, as is the case with solutions of hydrocarbons. The use of



solvents with a high boiling point is advisable, to avoid too firm hardening.

Experience has shown that bloom is not produced in coats containing less than 5% DDT, and other insecticides have been tested. A series of lacquer formulae with a lasting prolonged action, containing pyrethrum, was examined in the hope that they might be active against strains resistant to DDT and against some strains of fly in Sardinia. The results were not very encouraging. But on the other hand it was realized that the addition to pyrethrum of other substances, such as BHC and piperonyl butoxide, reinforces its toxicity, particularly with regard to strains resistant to DDT. Generally speaking, it was possible to conclude that the volatile insecticides have interesting properties since, in contrast to the solid insecticides, their toxicity is maximal with coats of fresh preparations; and that this diminishes in the course of time. Thinking that the presence of new molecules might have an influence on the toxicity of these volatile insecticides, mixtures were prepared containing aldrine (2%), BHC (2%), « C » acid, dieldrine and DDT. A kind of synergism existed among these different substances, the last three augmenting the apparent toxicity of the first two.

The author describes the differences in toxicity of these products, according to the nature of the surface upon which they are applied. He stresses the specific toxicity of these mixtures for certain groups of insects. He discusses the insectifuge value of the coats, and the service which can be rendered by pyrethrum, costly though it is, in the manufacture of these preparations.

Alluding to the question of practical application, and to co-operation between manufacturers of lacquers and manufacturers of insecticides, the author gives the information that certain domestic wall-papers and certain packing papers are now coated with insecticidal lacquers. Careful experiments have been carried out in ships' galleys and stores, where flies, cockroaches and maggots were eliminated in a few days in the presence of insecticidal coats. It seems probable that the latter can now be employed in places and on surfaces where insects habitually congregate.

Industry could make available coatings which would remain active for months, perhaps for years, despite frequent washing. In well-ventilated places, the dangers of human intoxication are minimal. This procedure would appear to be economic only when used for a long time, nine months at least. Other procedures, such as the impregnation of strips of paper suspended along the walls, might be preferred



in certain cases. Coats of insecticidal resin applied on metal nets or at the bottom of tubs of water might play a larvicidal role in the campaign against mosquitoes, by adding a certain proportion to insecticides in small pools of stagnant water. It would also be possible to investigate the use of insecticidal coats for buildings; this would have the advantage of avoiding repeated powdering or spraying, and of making insecticidal potency independent of the type of surface.

The author indicates the approximate price of these preparations, a price which cannot easily be compared with that of spraying according to simpler methods, and which depends on different factors. The advantage of coatings containing insecticidal resins would be that spraying could be eliminated — and in consequence all the variables which accompany current applications of long-acting insecticidal treatment.

**Zusammenfassung.** — Eine der aktuellen Fragen bei der Herstellung von Insektiziden mit Dauerwirkung ist die Entwicklung stabiler Träger, die imstande sind, das Insektizid mehrere Monate hindurch bei höchster Wirksamkeit zu erhalten. Mit Insektiziden gemischte Anstriche, Lackierungen und Presstoffe sind in den letzten Jahren als Verkleidung für Holz, Metall und andere Stoffe angewandt worden.

Die vorliegende Arbeit berichtet über die mit einem Stoff Carbamidformaldehyd ausgeführten Untersuchungen, der als Träger für Insektizide gegen Fliegen und Mücken gebraucht wurde. Mittels verschiedener Formeln wurde versucht, die Insektiziden mit den Schutz-Eigenschaften zu vereinigen, um eine Industrieherstellung des Verkleidungsmaterials und eine allgemeine Ingebrauchnahme desselben zu ermöglichen.

Nach mehr oder weniger langer Zeit erscheint an der Oberfläche bestimmter Lacke oder Harze, denen DDT oder ein anderes festes Insektizid beigegeben ist, eine kristallinische Auswitterung. Diese Auswitterung kommt daher, dass das DDT nach der Oberfläche strebt, und bildet sich spontan auf der Oberfläche der Verkleidung oder infolge der Insektentätigkeit. Wird die Auswitterung durch Trocknen und Waschen beseitigt, erscheint sie bei einigen Überzügen spontan von neuem. Die Übersättigung mit DDT reicht nicht aus, um diese unerklärliche Erscheinung zu erklären. Die Toxizität des Überzugs hängt von dieser Auswitterung ab.

Nachdem der Verfasser verschiedene Typen Firnisse, Lacke und Harze auf ihre Dauerhaftigkeit und ihren Toxizitätsgrad, sowie auf die optimalen Mengen des ihnen zuzufügenden Insektentötungsmittels

geprüft hat, beschreibt er eingehend die Stoffe aus Ureaformaldehyd, die die besten Ergebnisse zeitigen.

Die Versuche über die Toxizität des Überzugs — bei denen man neben die Wände, die mit diesen Lacken bedeckt sind, Insekten in Käfigen oder Petrischalen stellt und dann den Sterblichkeitssatz feststellt — sind sehr unterschiedlich und die von den verschiedenen Verfassern erhaltenen Ergebnisse sind schwer vergleichbar. Der von dem Verfasser für seine Experimente verwendete Stoff hat folgende Formel:

|                                   |      |               |
|-----------------------------------|------|---------------|
| Carbamid-Formaldehyd-Harz BE510 . | 50   | Gewichtsteile |
| Harz mit Rizinusöl-Alkalien BA502 | 50   | Gewichtsteile |
| Butylalkohol . . . . .            | 27,5 | Gewichtsteile |
| Xilol . . . . .                   | 27,5 | Gewichtsteile |
| Insektizid . . . . .              | 12   | Gewichtsteile |

Der Gehalt an Insektizid beträgt 20% des Gewichts der festen Bestandteile. Durch Säure oder Wärme oder durch beides zusammen wird es erhärtete.

Von den hauptsächlich dabei verwendeten Insekten, *Musca domestica* und *Aedes aegypti*, vertritt die erstere den Typ, der sich durch Laufen und Fliegen, die letztere die Art, die sich im Wesentlichen durch Fliegen, fortbewegt.

Die insektiziden Eigenschaften der Lacke bei Eintrocknung und Erhärtung wurden untersucht. Härtere Lacke erwiesen sich weniger toxisch auf Grund einer geringeren kristallinen Fluoreszenz an der Oberfläche. Die Toxizität der Lacke für *Aedes* wuchs mit ihrer Geschmeidigkeit an. Die Toxizität sehr harter Lacke nahm auch nach zwei Monaten nicht zu. Der Verfasser berichtet von den Ergebnissen mit verschiedenen Überzügen, die unterschiedliche Mengen « Erhärtungsstoffen » und « Weichmacher » enthielten. (Bei Bewertung der Dauer muss man die Wirkung in Betracht ziehen, die nach dem Verlust an DDT infolge Beseitigung der Fluoreszenz durch Waschen und Trocknen der Oberfläche bleibt). Er untersuchte ausserdem die Wirkung der ultravioletten Strahlen, die manchmal zum Erhärten verwendet werden. Die ultravioletten Strahlen vermindern die Fluoreszenz und somit die Toxizität, sie haben jedoch nur Oberflächenwirkung. Sie verringern, wie im Falle der Kohlenwasserstofflösungen, die Toxizität des DDT selbst nicht. Die Anwendung von Lösungsmitteln mit hohem Siedepunkt ist ratsam, um eine zu starke Erhärtung zu vermeiden.

Die Erfahrung hat gezeigt, dass die Fluoreszenz in den Überzügen, die weniger als 5% DDT enthalten, nicht auftritt, und man hat daher

andere Insektentötungsmittel ausprobiert. Eine Reihe von Formeln für Lacke mit gleichbleibender anhaltender Wirkung, die Pyretrum enthalten, wurde zusammengestellt in der Hoffnung, dass sie gegen DDT-resistente Stämme, wie zum Beispiel einige Fliegenrassen in Sardinien, wirksam seien. Die Ergebnisse waren nicht sehr ermutigend. Andererseits jedoch wurde festgestellt, dass, wenn dem Pyretrum andere Stoffe wie zum Beispiel BHC und Piperonil-Butoxyd beigegeben wurden, die Toxizität besonders gegenüber den DDT-resistenten Stämmen erhöht wurden. Ganz allgemein konnte man wahrnehmen, dass die flüchtigen Insektizide interessante Eigenschaften aufwiesen; denn im Gegensatz zu den festen Insektiziden war ihre Toxizität in frisch bereiteten Überzügen am grössten und verringerte sich im Laufe der Zeit. In der Annahme, dass die Anwesenheit neuer Moleküle die Toxizität dieser flüchtigen Insektenvernichtungsmittel beeinflussen könnte, wurden Mischungen hergestellt, die Aldrin (2%), BHC (2%), « C »-Säure, Dieldrin und DDT enthalten. Zwischen diesen verschiedenen Stoffen besteht eine Art Synergie, insofern als die drei letzteren die scheinbare Toxizität der ersten beiden erhöht.

Der Verfasser erklärt die Unterschiede in der Toxizität dieser Produkte je nach der Art der Oberfläche, auf die sie aufgebracht werden. Er betont die spezifische Toxizität dieser Mischungen für gewisse Insektengruppen. Er bespricht den insektiziden Wert von Überzügen, und den Dienst, den Pyretrum, selbst wenn es kostspielig ist bei der Herstellung dieser Präparate leisten kann.

Der Verfasser berührt sodann die Frage der praktischen Anwendung und der Zusammenarbeit zwischen Lack- und Insektenvernichtungsmittel-Fabrikanten und erwähnt, dass gewisse Tapeten für Wohnungen und gewisses Einpackpapier mit insektentötenden Lacken überzogen sind. Genaue Versuche wurden in Schiffsküchen und -Speicherne durchgeführt, wo Fliegen, Schaben und andere Insekten durch insektentötende Überzüge in wenigen Tagen ausgerottet wurden. Es ist wahrscheinlich, dass solche Wandverkleidungen in Lokalen und an Oberflächen, wo Insekten vorzugweise anfliegen Anwendung finden werden.

Die Industrie kann Verkleidungen anbieten, die Monate, vielleicht sogar Jahre lang trotz häufigen Waschens wirksam bleiben. An gutgelüfteten Orten sind die Intoxikationsgefahren für den Menschen minimal. Dieses Kampfmittel erweist sich nur für langanhaltenden Gebrauch — wenigstens für neun Monate — wirtschaftlich in gewissen Fällen kann man andere Verfahren vorziehen, zum Beispiel indem man Papierstreifen tränkt und dann an den Wänden entlang aufhängt. Wenn man auf Metallnetzen oder auf dem Boden von Teichen Auskleidungen mit



insektenschädlichen Harzen anbringt, könnte man im Kampf gegen die Mücken eine larventötende Wirkung hervorrufen, indem man bei wenig ausgedehnten stehenden Wässern einen gewissen Gehalt an Insektenvernichtungsmittel aufrecht erhält. Man kann auch den Gebrauch von Verkleidungen in Gebäuden vorschlagen, was den Vorteil hätten, wiederholte Verstäubungen und Ausspritzungen zu vermeiden und das Insektenvernichtungsvermögen von dem Typ der Oberfläche unabhängig zu machen.

Der Verfasser gibt den ungefähren Preis dieser Präparate an, welchen man nicht leicht mit dem der einfachen Spritzmittel vergleichen kann, und der von verschiedenen Faktoren abhängt. Die Auskleidungen mit insektentötenden Harzen hätten den Vorteil, die Ausspritzungen überflüssig zu machen, wobei auch alle Faktoren entfallen die zur Zeit bei Anwendung von Insektenvernichtungsmitteln mit Dauerwirkung auftreten.

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#### INTRODUCTION.

World War II saw the replacement of the chemically unstable vegetable insecticides by the stable synthetic insecticides like DDT and BHC. This feature of chemical stability introduced a new concept into methods of controlling flies and mosquitoes, i.e. the use of insecticidal residues which retained contact toxicity up to several months after application to surfaces of different kinds, in contrast with the former practice of at least daily use of space-sprays from hand sprayers.

Diluents of different kinds have been used as vehicles for applying residues either as solutions, suspensions or dry dusts. Experience under practical conditions has shown the effective duration of DDT residues to vary considerably and to be often much shorter than might have been expected from what is known of its chemical stability. It might be said that the insecticide was not in a vehicle which enabled full use to be made of the potential duration of the chemically stable DDT. In recent years, therefore, greater attention has been given to the characteristics of vehicles for insecticidal residues not only to extend as long as possible the duration of insect control from each application but also to improve the degree of potency of the residues. The alarming incidence of strains of resistant flies has underlined the latter aspect.

The next stage in the evolution of insecticidal residues might therefore be considered as the development of stable vehicles capable

of maintaining the stable insecticides in a condition of maximum potency over periods of many months. The media which were first considered for this role were household paints and distempers, and these were followed by synthetic resins developed in recent years for a wide range of industrial usage as surface coatings for wood, metal and other surfaces. On the whole, while many coating compositions have been prepared which contained much insecticide none can be said to have been efficient insecticidally when compared with the residues from wettable powders or oil solutions, and this has been reflected in the failure of these paints in competition with traditional types of residues.

In the following paper some account is given of studies with urea-formaldehyde resin as a vehicle for semi-permanent insecticidal coatings against flies and mosquitoes. Although emphasis has been laid on the biological requirements of such coatings, a compromise has been reached with the requirements for good protective coatings *per se* by basing the formulations on suggestions made by the research department of British Industrial Plastics Ltd. out of their great experience of urea-formaldehyde resin surface coatings. This co-operation ensured that recommended insecticidal formulations were capable of easy production on an industrial scale, if required, and would not be unknown to industrial users of urea resin coatings on metal, wood or other surfaces.

#### RECENT DEVELOPMENTS IN INSECTICIDAL COATINGS.

##### 1) *Coating vehicles.*

West and Campbell (<sup>1, 2</sup>) began investigations in the United Kingdom by incorporating DDT into several types of coating, e.g. dry distemper, oil-bound water paint, white lead oil paint and synthetic varnish enamel, and then went on to flat oil paint, coumarone resin and oil varnish. LINDQUIST (<sup>3</sup>) and his co-workers in USA added DDT to a calmine cold water paint. GILMOUR (<sup>4</sup>) in Australia tested DDT in water paint, emulsion-type paint of oil in water, a flat oil paint and glossy enamel. BARNES (<sup>5</sup>) in the United Kingdom extended the studies into distempers and HARRISON (<sup>6</sup>) in New Zealand added to the knowledge of flat oil paints. In the USA again BLOCK (<sup>7, 8</sup>) made a study of 33 compounds as vehicles for insecticidal coatings, adding BHC, pyrethrum, and other insecticides to the DDT used exclusively by earlier workers.

The insecticide was incorporated usually by simple grinding into the vehicle, but in one or two cases by solution into the paint solvents.

In reviewing the results of the insecticidal tests carried out by these workers, the coatings can be divided into those which were non-insecticidal; those which were poorly insecticidal at first but increased in potency with age, and lastly those which were highly toxic within a few days of preparation. The most toxic coatings developed a visible surface bloom of DDT crystals.

BARNES <sup>(5)</sup> showed that distempers, in which the DDT was incorporated as a solid suspension, maintained the same low level of potency even after ageing.

The development of surface crystals of DDT was noted in coumarone resin films by WEST and CAMPBELL, in flat oil paints by GILMOUR <sup>(4)</sup> and HARRISON <sup>(6)</sup>, and in several synthetic resin finishes by BLOCK <sup>(7, 8)</sup>. It was compared with the bloom of DDT crystals observed by PARKIN and GREEN <sup>(9, 10)</sup> to be produced from the supersaturated residues of kerosene solutions of DDT on absorbent wall board. It was also noted that the bloom followed insect activity on the treated surface.

In his investigation of numerous coating compositions BLOCK agreed with previous workers that the toxicity of effective coatings increased with the concentration of insecticide, with age and the consequent appearance of crystals on the surface. Regeneration of the crystalline bloom after cleaning the surface did so only partially from PARKIN and GREEN's kerosene deposits but was very marked with coumarone resin films, flat oil paints and several of the synthetic resins.

Although the appearance of surface crystals in some films was considered to be due to the DDT being in a supersaturated state, no explanation could be found for the failure of surface blooming in oil paints or enamels. GILMOUR <sup>(4)</sup>, after ensuring that the enamel solvents were supersaturated with DDT, considered that the absence of surface crystals and consequent poor insecticidal action, was due to some unknown factor which interfered with the migration of DDT to the surface. BLOCK observed variations of a similar type in some of the media examined by him, and added the observation that the ageing needed to mature different coatings to maximum toxicity ranged from one week to two years. Because the most toxic concentration of DDT used by previous workers had been about 20 per cent on the weight of solids (excluding inert fillers and pigments), BLOCK adopted this concentration as a standard for all his vehicles. With an application rate of one ounce (28 g) of solids per square yard, this gave about 600 mg of DDT per sq. ft. HARRISON used the rate of about 700 mg DDT per sq. ft. from the so-called "5%" DDT in flat oil paint; while WEST and CAMPBELL



applied flat oil paint at a rate which gave a calculated dosage of 2.66 mg DDT per sq. cm or about 2,000 mg per sq. ft.

Summarizing the observations by previous workers on the physical characteristics of insecticidal coatings, it appeared that the latter could be divided into two groups:

1. Vehicles in which the insecticide was held in solid suspension in a static condition, e.g. in distempers. In this group the insecticide showed no migration to the coating surface nor an increasing toxicity with age.

2. Vehicles in which the insecticide was held in supersaturated solution in a dynamic condition. This second group fell naturally into two divisions:

- (a) those media which allowed a progressive migration of DDT to the surface as crystals with a corresponding increase in toxicity upon ageing;

- (b) those media in which the DDT, although in a supersaturated solution, did not migrate to the surface but rather remained below the coating surface with a consequent low level of toxicity.

Urea-formaldehyde resin was one of the most promising materials tested by BLOCK and this was selected for further investigation because it was considered a versatile material, freely available, in common industrial usage and with a far wider range of uses than the usual paints on surfaces like glass, metal, wood, brick or paper by spraying, dipping, brushing or roller-coating.

## 2) *Bio-assay methods.*

The testing techniques used by previous workers varied so much that few direct comparisons can be made of the potencies of similar vehicles. The housefly has been the test insect generally used although WEST and CAMPBELL used bed-bugs and roaches and BLOCK also used roaches for a few tests. Mosquitoes were not used.

All workers have adopted rather similar methods of exposing flies to the test surfaces. This has been by assembling boxes or cages approximately of one foot cube in which from one to five walls were lined with plywood painted with the test coating. BARNES was an exception in using petri dishes to confine flies on to insecticidal distempers applied to board. GILMOUR used a second test in which single flies were enclosed in wooden cells one inch cube coated completely on the inside with the test paint.

The numbers and condition of flies used also varied. WEST and CAMPBELL placed 100 pupae in a glass dish inside the cage and noted kills daily for up to seven days. Other workers inserted about 50 adult flies in the test cages and left them there for varying periods up to the point of 50% or even complete knock-down, up to one hour, or even up to 24 hours. After considering the methods employed by previous workers BLOCK used the time required for 50% knock-down of four to six day old flies in wooden cages as the criterion of comparative toxicity.

The possible significance of biological factors affecting the tests was considered by WEST and CAMPBELL and by GILMOUR. The former, who were the only workers to record field trials with insecticidal paints, considered that DDT in flat oil paint was not repellent to flies. They arrived at this opinion after observing that flies crawled freely over the painted windows of a test room.

But GILMOUR, who used a cage in which only one wall was coated with the DDT paint, noted a strong repellency of the DDT to flies, because the number of flies resting at any one time on the treated panel was very low, e.g. about 0.5 as compared with 17 on the control panel during spot checks. Again, those flies which did alight on the bloomed DDT paint left again almost immediately. Using his single fly method GILMOUR found that contact times of nine seconds were necessary to kill 50% of female flies, so that momentary contacts on DDT films would not be likely to give satisfactory results under practical conditions.

It is evident from the variety of tests used that flies would require numerous contacts with DDT coatings to ensure kills and that if possible flies would avoid resting on DDT residues. Mortalities obtained by different methods therefore varied considerably. BARNES found that only 40% of flies were killed after a 15 minute contact on a 20% DDT in distemper under petri dishes, while HARRISON noted 100% knock-down after leaving flies up to 20 minutes in a wooden cage completely lined with a bloomed DDT paint.

In one of the few field trials carried out with coatings WEST and CAMPBELL found that in a canteen painted out with a DDT paint, although many flies were killed, the rate of kill was too slow to reduce the fly nuisance. It was not stated whether or not a bloom of DDT crystals appeared on the canteen walls. HARRISON suggested that because maximum potency of flat oil paints was not reached until crystals

appeared, the painted walls should be wiped down with a duster to ensure crystal formation. No experiments have been carried out under practical conditions to determine how important this factor would be.

In reviewing the bio-assay techniques employed the impression is gained that the workers were searching for one which would perhaps truly reflect practical conditions. This probably accounted for the lack of uniformity in detail of the techniques which makes comparisons difficult. The field trials based on the laboratory methods did not give encouraging results and this may not be considered surprising in view of GILMOUR's significant observations on the repellent properties of DDT coating most toxic to flies. It seemed certain that under practical conditions flies would tend to avoid surfaces coated with crystalline DDT. To what extent repellency might operate with other insecticides was not known.

## MATERIALS AND METHODS.

### 1) *Chemical.*

The formulations used were based generally on BE610 urea-formaldehyde resin and BA502 castor oil alkyd resin as a plasticizer.

BE610 is an unmodified urea resin; colourless, containing 60% solids in butanol; specific gravity 1.05; acid value 2; viscosity at 25° C 50 Stokes; flash point 78° F. It is miscible in all proportions with higher alcohols, ethers, ketones and esters. Although compatible with tricresyl phosphate and other solvent type plasticizers, the non-drying alkyds are the best for general use, the proportions of which are varied for industrial coatings from 25% to 300% calculated on the resin solids. For most purposes equal parts of resin and plasticizer will give a good film flexible enough for application to metal articles not subject to bending.

BA502, a castor oil alkyd, was generally used as the plasticizer for the urea resin. It has a slight straw colour; contains 60% solids dissolved in xylol; specific gravity 1.05; acid value 25-30; viscosity at 25° C 150 Stokes; oil length 40; flash point 68° F. It is soluble in aromatic hydrocarbons but not in esters. A mixture of four parts xylol to one of butanol was used for thinning this resin (as well as a cleaning medium for brushes). The acid number of the resin is high enough to assist in curing the urea resin without affecting any pigments which might be used.



A standard lacquer was used of the following type:

|                                |      |                 |
|--------------------------------|------|-----------------|
| BE610 Urea-formaldehyde resin  | 50   | parts by weight |
| BA502 Castor oil alkyd resin . | 50   | parts by weight |
| Butanol . . . . .              | 27.5 | parts by weight |
| Xylol . . . . .                | 22.5 | parts by weight |
| Insecticide . . . . .          | 12   | parts by weight |

This made a clear, free-flowing lacquer containing 40% solids which was stable to long storage at room temperatures ranging from freezing up to 85° F. The proportion of insecticide was always based on the weight of resin solids which thus allowed direct comparisons to be made between the dry coatings made from different formulations: the one quoted above would give a solid coating containing 20% by weight of insecticide. Because the resin solutions were so viscous the insecticide was first dissolved in the added solvents, before being added to the resin mixture. The insecticide was always completely dissolved in the lacquer which thus appeared clear or translucent.

The lacquers were applied to test surfaces by paint brush, spray gun or by flowing on a measured quantity. The weight of coating was kept as closely as possible to that generally recommended, one ounce (28 g) per square yard of solid coating.

Drying or hardening of the coatings was achieved mostly by the use of acid accelerators or by heat, or by a combination of both methods. A satisfactory air-dried coating from the formulation given above was made by the addition of one part accelerator to 20 parts of lacquer just before use. This accelerator, consisting of 10% concentrated sulphuric acid in butanol is referred to as AC54. After the addition of the accelerator the mixture had a pot-life of several hours.

A number of well-known insecticides were used in the investigations including DDT, gamma BHC, dieldrin, aldrin, pyrethrum and allethrin. These were always added as proportions of the active isomer whether used in the pure or technical grades.

## 2) Entomological.

*Musca domestica* and *Aedes aegypti* were reared as test insects according to established methods, and used at from four to seven days and one day (unfed) respectively. In these investigations into insecticidal coatings a number of insect species were used which were classified into groups according to their method of locomotion. *Aedes* was classified as a purely aerial or non-pedestrian type and *Musca* as

an aerial/pedestrian species which normally walks as freely as it flies. Although both species are normally very active they are so in very different ways. *Aedes* moves about almost entirely by flight, and may be said to make contact with surfaces only by means of a number of separate and distinct landings and not by walking at all. Such a species may be expected, therefore, to be affected far more by the vapour action of a volatile insecticide than by a non-volatile insecticide. *Musca* in contrast, by walking freely over insecticidal residues is likely to be affected by non-volatile residues more readily than *Aedes*.

The significance of the part played by insect activity in relation to the toxicity of insecticidal residues or sprays has been indicated by DAVID and BRACEY and BUSVINE and BARNES, who showed that the more an insect flew in an insecticidal mist or walked over an insecticidal deposit, the more insecticide was picked up and the greater the subsequent kill.

The methods used for exposing the insects to the residues were influenced by the type of locomotion as well as by the special characteristics of the insecticides. Emphasis was laid on factors which were considered to be of the greatest importance as a guide for practical application, although it was considered that no laboratory test could replace properly controlled field trials.

For contact periods of very short duration with *Aedes* an apparatus (Plate 1) was used similar to one devised by KENNEDY and AINSWORTH (unpublished). This worked on the principle of enclosing a number of mosquitoes under a light perspex funnel, widest diameter 2.5 inches by 2.5 inches high, which rested on a polished tufnol slipper, measuring 4 x 3 inches. The latter was held by a trigger against a tensed spring. When the trigger released the slipper from its anchorage it was whipped from under the feet of the mosquitoes, allowing the latter to fall on to the test surface placed immediately beneath the funnel. After the necessary contact time had elapsed as measured by stop-watch, the funnel and test panel were held in the left hand, a light CO<sub>2</sub> anaesthesia applied and the insects transferred to the recovery cage via the narrow end of the funnel. The recovery cage was a cylinder of metal gauze 3 inches high by two inches diameter with steel top and bottom, of the type described by DAVID (1946). Mortalities were estimated after 24 hours. The apparatus was designed for aerial insects and was quite useless for *Musca* which walked about too much. It allowed fairly large numbers of mosquitoes to be exposed to residues together for short contact periods, so that many tests could be made quickly with reasonable repeatability. A serious defect of the method was the un-

doubtedly exaggerated picture it gave of the potency of volatile insecticides because of the small volume of space enclosed by the funnel. The method did, however, allow considerable differences to be shown in the relative potencies of different residues when using contact times of up to one hour. Residues which required longer contact times for good kills were not considered likely to be of much practical use. About 40 mosquitoes were used per test.

*Musca* was usually tested by being confined under 7 cm petri dishes, usually for short contact times. About 10 flies were used per test.

The petri dish method was also used to make easy and rapid screening tests of candidate formulations by noting the knockdown rate of flies or mosquitoes.

Special consideration was given to the toxicity of vapour arising from coatings. This was done by enclosing flies or mosquitoes within the upper two of three perspex rings (diameter 2.5 inches by height one inch) arranged in tiers. The top ring was closed by copper gauze held in place by an elastic band. The base of the middle ring was similarly closed, while the basal ring served simply as a stand to keep the insects from touching the coating. By this simple device, toxic vapours could pass up through the cylinder formed by the rings, amongst the insects, and finally escape freely into the surrounding air. The great difference in the vapour phase toxicity of volatile insecticides like BHC contrasted strongly with the absence of such toxicity of DDT residues.

The importance of the number of insects per unit area upon the resultant kills was examined with special reference to aerial insects. All laboratory testing techniques are essentially unnatural as environments for insects but some techniques do try to cater for the idiosyncrasies of behaviour of particular species. Because BUSVINE and BARNES had shown that increased walking activity caused greater kills, tests were made to check if the testing method used here would cause higher kills of *Aedes* when large numbers of mosquitoes were confined on residues. The repellency of DDT noted by GILMOUR and KENNEDY (<sup>14</sup>) together with the effect of so many males and females in close proximity tended to make *Aedes* behave quite unnaturally in the testing apparatus. As *Aedes*, like other mosquitoes, walks only rarely, and in nature very low numbers per unit area might be expected on resting surfaces treated with residues (<sup>15</sup>), tests were made using definite numbers of insects, with the sexes kept separate.

Fibre-board plaques 4 × 4 inches were sprayed with 100 mgm/sq, ft of a commercial suspension of DDT crystals (DE DE TANE), stated to have a mean length of 6 microns by 1 micron thick. Males and females



were kept to separate plaques, and four replicates made of each point. The mosquitoes were collected by aspirator, lightly knocked-down by CO<sub>2</sub> and separated into lots of 10, 20, 40, 80 on the tufnol slippers and under the Perspex funnels. After recovery, care was taken to use the smaller lots of insects first in order to avoid possible exaggeration of effects due to the larger batches of insects removing greater proportions of DDT crystals. Results are shown in Table 1-a. From the data in Table 1, two features are apparent (1) the increase in kill which accompanied increase in numbers and (2) that males were more resistant to the residue than females. During the contact periods the larger groups were noticeably more active than the smaller ones. It appeared that with two minute contacts or less only a change of formulation or insecticide would be likely to effect a change in the toxicity of the residues. The reversal in susceptibility of males and females only occurred with short contact times because when males and females were confined on DDT residues until knock-down occurred the males were affected slightly sooner than the females. CUTKOMP<sup>(16)</sup> has also observed that females were more resistant than males in similar tests. DAVID and BRACEY found that when exposed to insecticidal mists, the males were more susceptible than the females. This reversal of susceptibility was noted also by REID<sup>(17)</sup> using a different testing technique with *Anopheles vagus*.

TABLE 1.a.

*The influence of insect number per test on the toxicity  
of a DDT residue to Aedes aegypti*

| Contact time | Sex    | Number per test | Average % kill |
|--------------|--------|-----------------|----------------|
| 2 minutes    | Male   | 10              | 4              |
| » »          | »      | 20              | 10             |
| » »          | »      | 40              | 14             |
| » »          | »      | 80              | 14             |
| » »          | Female | 10              | 23             |
| » »          | »      | 20              | 34             |
| » »          | »      | 40              | 45             |
| » »          | »      | 80              | 47             |
| 4 »          | Male   | 10              | 10             |
| » »          | »      | 20              | 34             |
| » »          | »      | 40              | 52             |
| » »          | »      | 80              | 96             |
| » »          | Female | 10              | 39             |
| » »          | »      | 20              | 57             |
| » »          | »      | 40              | 97             |
| » »          | »      | 80              | 100            |

Except in special tests, insects were exposed to residues at 25° C and approximately 70% R.H. Coatings which were not stored under those conditions were taken into the test room at least half an hour before beginning the tests.

#### THE IMPORTANCE OF HARDNESS ON THE BEHAVIOUR OF DDT IN UF COATINGS.

Urea formaldehyde resin coatings are usually cured in order to produce a sufficiently hard and durable finish and this curing is effected by heating the film or by the action of acid accelerators, or by a combination of both methods. BLOCK, who first described the incorporation of insecticides in urea resin, did not state what method he used for hardening these coatings. In the present investigations, a series of films were prepared by British Industrial Plastics Ltd., on tinplate and examined for insecticidal action over a period. The following formulations were included in some preliminary tests:

|                              |         |
|------------------------------|---------|
| 1. BE 610 Urea resin . . . . | 500 gms |
| DDT (solid) . . . .          | 60 gms  |
| Butanol . . . .              | 20 cc   |
| Xylol . . . .                | 105 cc  |

DDT content 20% on the resin solids.

|                              |         |
|------------------------------|---------|
| 2. BE 610 Urea resin . . . . | 50 gms  |
| BA 502 Castor Oil alkyd . .  | 50 gms  |
| DDT (solid) . . . .          | 12 gms  |
| Butanol . . . .              | 7.5 cc  |
| Xylol . . . .                | 22.5 cc |

DDT content 20% on the resin solids.

In (1) the formulation was an attempt at what might have been used by BLOCK, while (2) is the type of plasticized urea lacquer found by experience in UK to give hard, mar-proof finishes whether hardened by heat or by acid accelerators.

Lacquers were prepared and cured in the following way:

- (1) E plus 5% accelerator AC 64 (calculated on resin solids). Air-dried 16 hours at room temperature.  
 F plus 3% accelerator AC 64, and stoved for one hour at 60° C.  
 C No accelerator, but stoved for 2 hours at 90° C.  
 I plus 2% accelerator AC 64 and stoved for half-hour at 90° C.
- (2) J<sub>1</sub> no accelerator, but stoved for 2 hours at 90° C.  
 J<sub>2</sub> plus 2% accelerator AC 64 and stoved for half-hour at 90° C.

The coatings were prepared in duplicate. When examined at a few days old and before tests were carried out, no surface crystallization was visible but some surface cracking was apparent on E & F.

Because flies and mosquitoes were not considered suitable for the purpose of giving a standard degree of surface stimulation to the coatings, it was decided to place 30 adult flour beetles (*Tribolium castaneum*) on each coating. The beetles were confined within perspex rings, and walked continuously until knocked down. For the first test, flour beetles were placed in the coatings for four hours and then taken off. A day later a bloom of DDT crystals showed in a circular area on E & F only. After a further interval, beetles were put on again but this time for 24 hours. When the insects were removed, all the coatings except I showed circular areas of crystalline bloom.

Although the coatings were subsequently cleaned with petroleum ether and cotton wool and exposed to flour beetles on several occasions, the I coatings failed to show surface crystals for many weeks. The coatings E, F, G and I from lacquer (1) were brittle, hard and tended to crack, and were not considered serviceable for practical purposes. Attention was therefore concentrated on formulation (2) which produced tougher coatings.

PARKIN and GREEN had indicated the increase of toxicity from DDT residues which followed the appearance of crystalline bloom. BLOCK had also, with other workers on surface coatings, noted that DDT crystalline bloom varied from one coating formulation to another. No one had yet shown how the appearance of bloom might be varied at will. *Musca* tested on the above coatings before the appearance of bloom gave the following results:

TABLE 1.

*Toxicity of UF coatings containing 20% DDT to Musca.*

| Coating        | Age in days | Contact time | Number used | % Kill<br>after 24 hrs. | Bloom |
|----------------|-------------|--------------|-------------|-------------------------|-------|
| E              | 10          | 1/2 minute   | 42          | 7                       | Nil   |
| F              | »           | »            | 45          | 18                      | Nil   |
| G              | »           | »            | 38          | 0                       | Nil   |
| I              | »           | »            | 42          | 0                       | Nil   |
| J <sub>1</sub> | »           | »            | 37          | 0                       | Nil   |
| J <sub>2</sub> | »           | »            | 42          | 0                       | Nil   |
| BE 610         | —           | »            | 45          | 49                      | Good  |



Following the induction of bloom by flour beetles, crystals were most evident on E, G and J, much less so on F and absent on I. *Aedes* put on for eight minutes gave percentage kills of 69, 0, 79, 0 and 43 respectively for E, F, G, I and J.

It appeared that the different curing given to the coatings had some effect on the degree and rate of crystallization.

As the curing affects the hardness of UF coatings it was assumed that the hardness might be controlling the emergence of DDT crystals (<sup>18</sup>). Experiments were therefore carried out with the plasticized UF lacquer used above but cured to different hardnesses as determined by the Sward Rocker Apparatus.

TABLE 2.

*Relationship between resin hardness and rate of knockdown of Musca exposed continuously to the resins under Petri dishes. Four replicates of 15-20 flies each.*

| Coating | Sward Rocker Units | Per cent DDT | 100% Knockdown after           | Crystal bloom |
|---------|--------------------|--------------|--------------------------------|---------------|
| D       | 28                 | 40           | 34 minutes                     | Heavy         |
| C       | 32                 | 20           | 45 minutes                     | Heavy         |
| B       | 36                 | 40           | 60 minutes                     | Faint         |
| A       | 46                 | 20           | 60% knockdown after 64 minutes | Poor to Nil   |

The flies, imprisoned under petri dishes on the coatings, were paralysed after periods of contact which increased with the hardness of the films, irrespective of the DDT concentration. Because the crystalline bloom was difficult to remove by washing with soap and water

TABLE 3.

*Effect of excessive hardness of UF resin coatings containing 20% DDT on the toxicity to Musca (with further ageing of Coating A)*

| Coating | Sward Rocker Units | Average time for 100% knockdown | Bloom       |
|---------|--------------------|---------------------------------|-------------|
| A       | 46                 | 37 minutes                      | Medium      |
| A1      | 48                 | 50 minutes                      | Poor        |
| A2      | 72                 | 66 minutes                      | Poor to Nil |
| A3      | 76                 | Not affected after 60 minutes   | Nil         |
| A4      | 78                 |                                 |             |

this was done by swabbing with cotton wool soaked in petroleum ether. Both D & C had regenerated heavy blooms after one week, B had barely perceptible crystals while A had apparently none. The two latter coatings developed well-marked blooms after seven weeks and were equal in toxicity to C & D.

A further set of coatings were prepared on tin-plates, using the same plasticized urea resin formulation but hardened to greater degrees up to 78 Sward Rockers units. Houseflies which were imprisoned on the coatings under petri dishes were less affected as the hardness increased.

Coatings A3 and A4 showed no surface crystal when examined under the microscope while A1 had a sparse bloom of DDT needles about five microns long, or much smaller than the crystals on the coating A.

*Aedes* were exposed to the coatings on the following day, when a slightly heavier bloom had appeared on A1 although A2, 3 and 4 showed no apparent difference.

TABLE 4.

*Rate of knockdown of Aedes in continuous contact with coatings of increasing hardness containing 20% DDT*

| Coating | Sward Rocker Units | Average time for 100% knockdown | Bloom       |
|---------|--------------------|---------------------------------|-------------|
| A       | 46                 | 80 minutes                      | Medium      |
| A1      | 48                 | 83 minutes                      | Poor        |
| A2      | 72                 | 95 minutes                      | Poor to Nil |
| A3      | 76                 | Not affected                    | Nil         |
| A4      | 78                 | Not affected                    |             |

The hardest coatings were non-toxic to *Aedes* while toxicity increased as the coatings got softer. After ageing for a further two months the harder coatings showed no increase in toxicity nor development of bloom.

#### OTHER METHODS OF CONTROLLING THE HARDNESS OF UF COATINGS.

##### 1) *Ratio of Urea resin to plasticizer.*

Earlier in this paper UF formulations were quoted in which a plasticizer was absent. These formulations produced coatings much

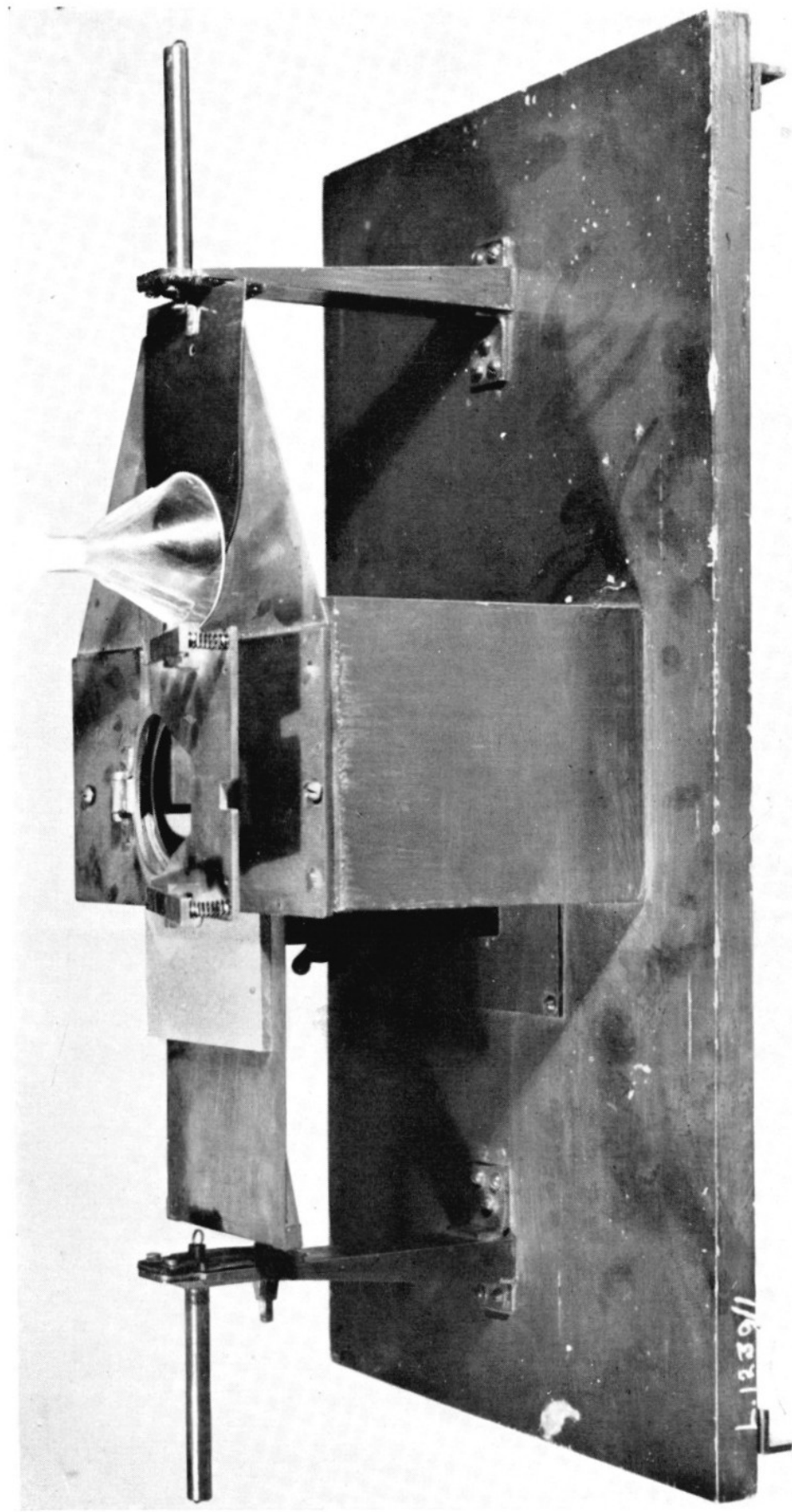


Plate 1. Fig. 1. - Apparatus for exposing flying insects to insecticidal residues.



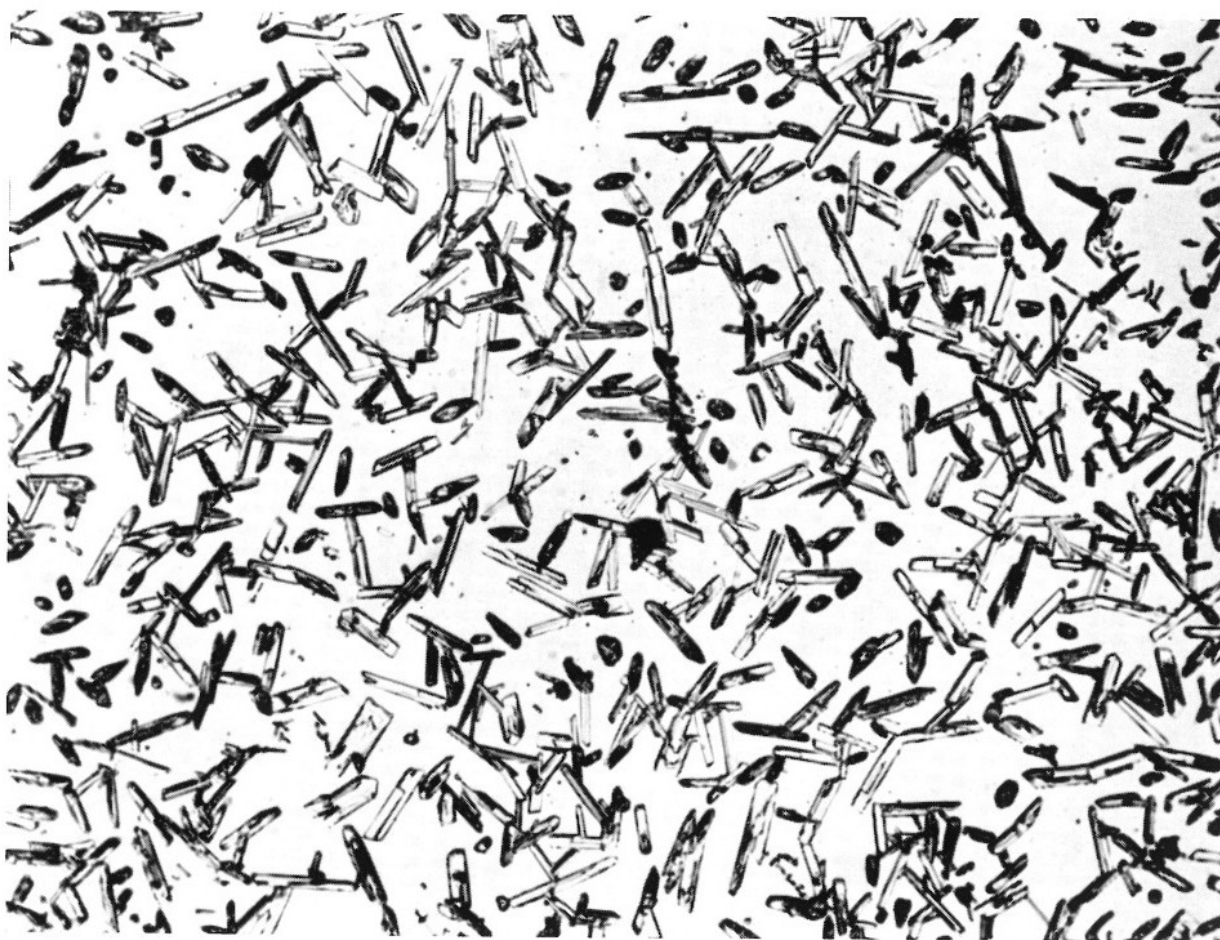


Plate 2. Fig. 2. -  $\times 120$  DDT crystals induced by *Tribolium* from air-dried coating containing Urea/Alkyd at 40/60.



Plate 2. Fig. 3. - As above, with Urea/Alkyd 60/40.

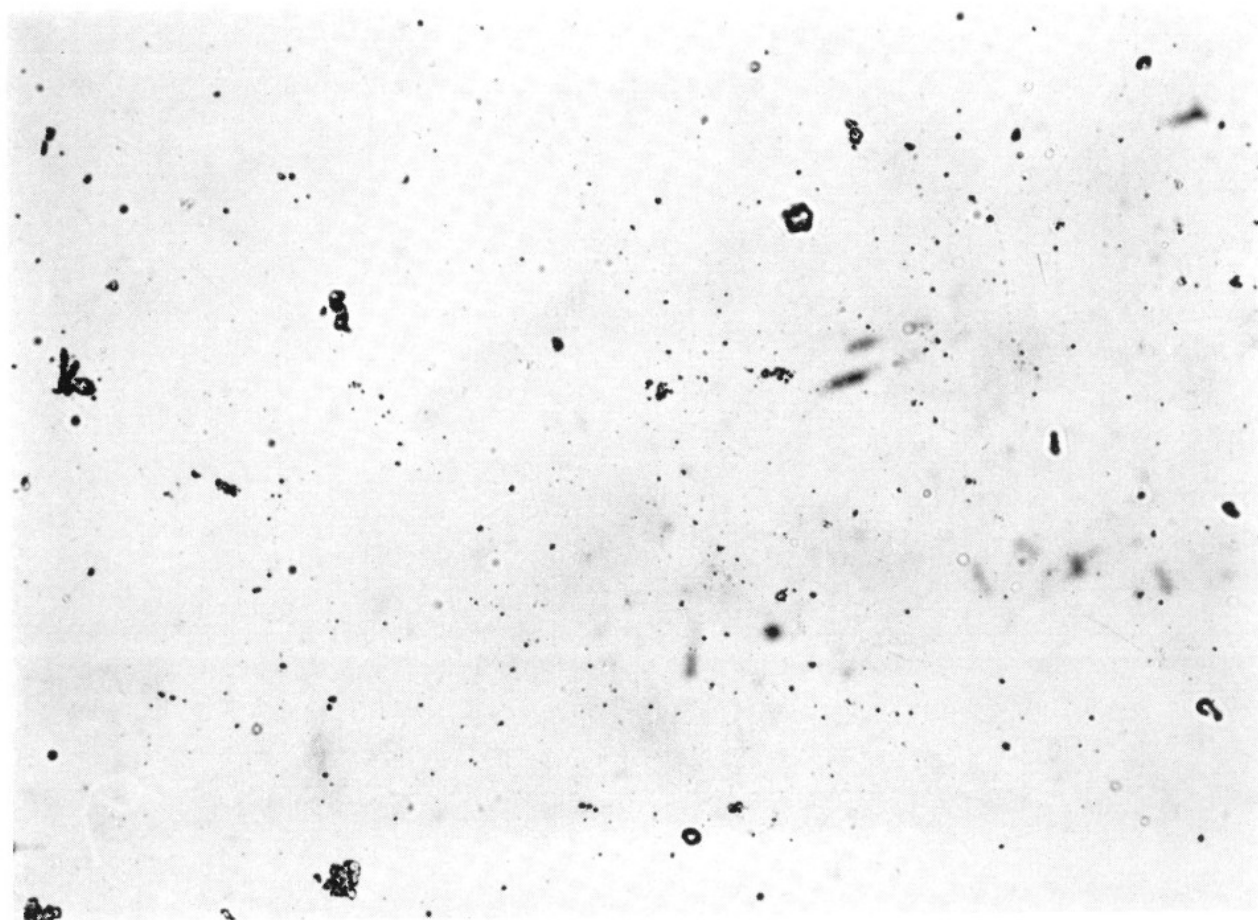


Plate 2. Fig. 4. - As above, with Urea/Alkyd 70/30.



Plate 3. Fig. 5 - DDT crystals in rows induced by *Glossina palpatis* on U/A 50/50.



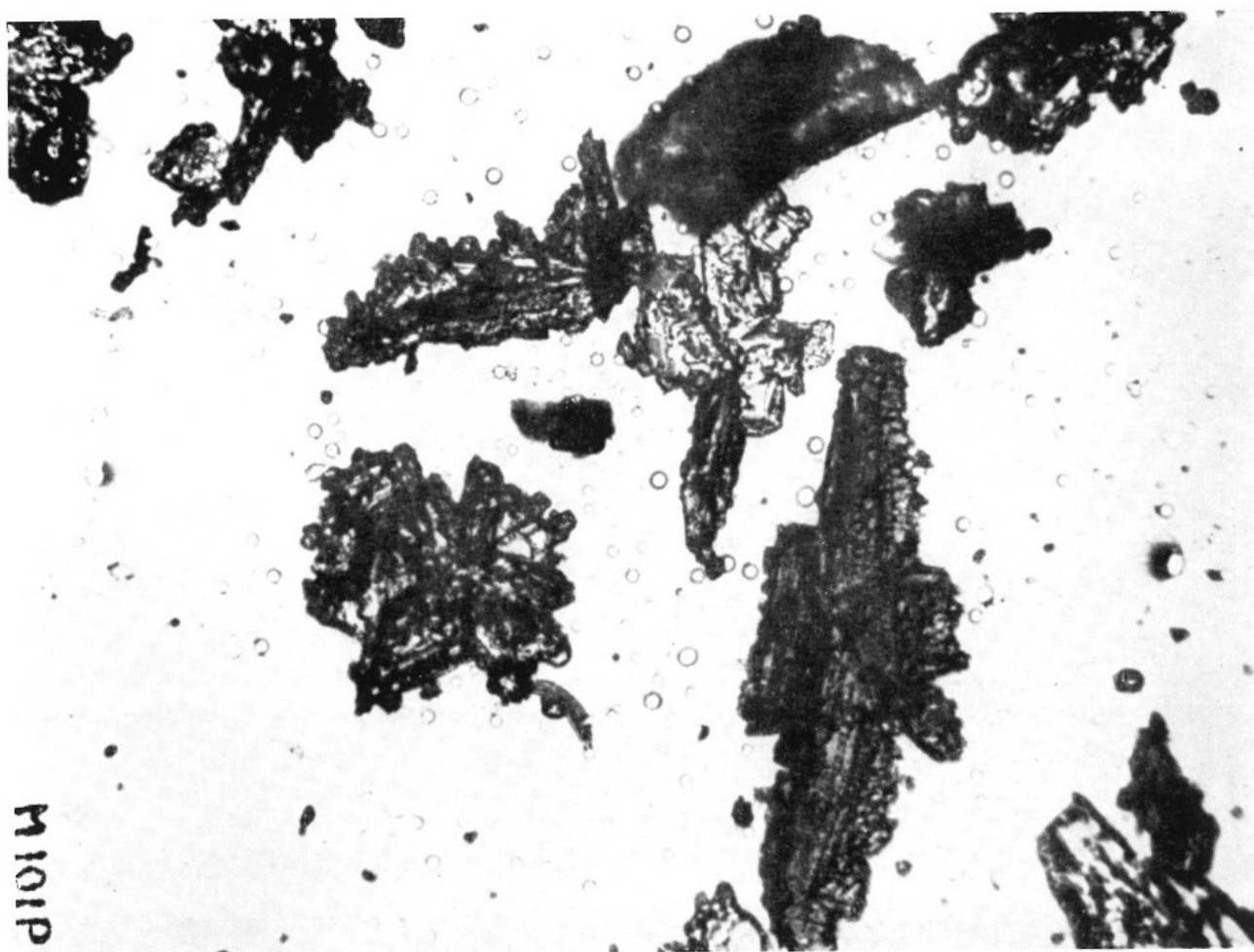


Plate 4. Fig. 6. - Aldrin crystals of spontaneous origin from 40 % concentration.

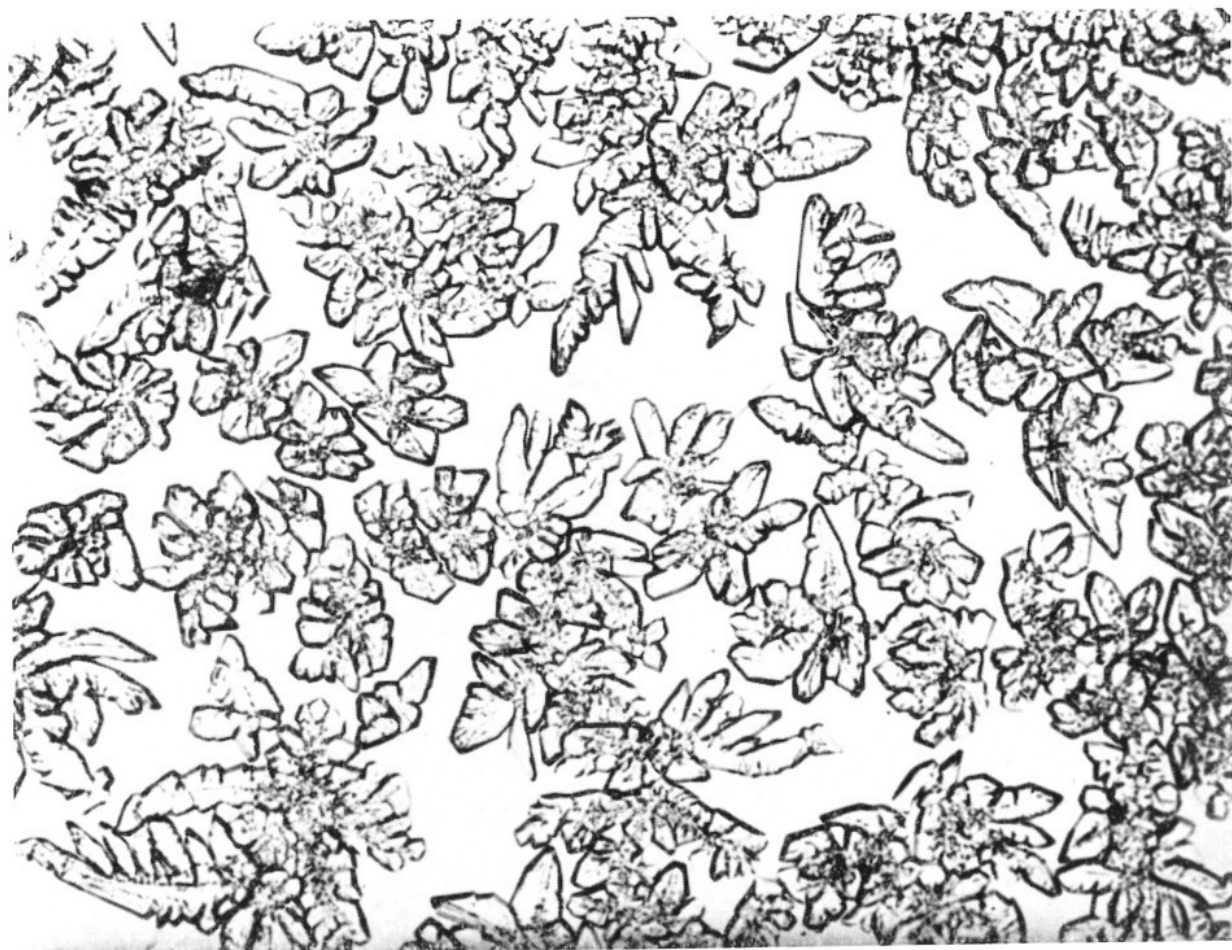


Plate 5. Fig. 7. - Crystals induced by Tribolium 20 % Isodrin in U/A 50/50.

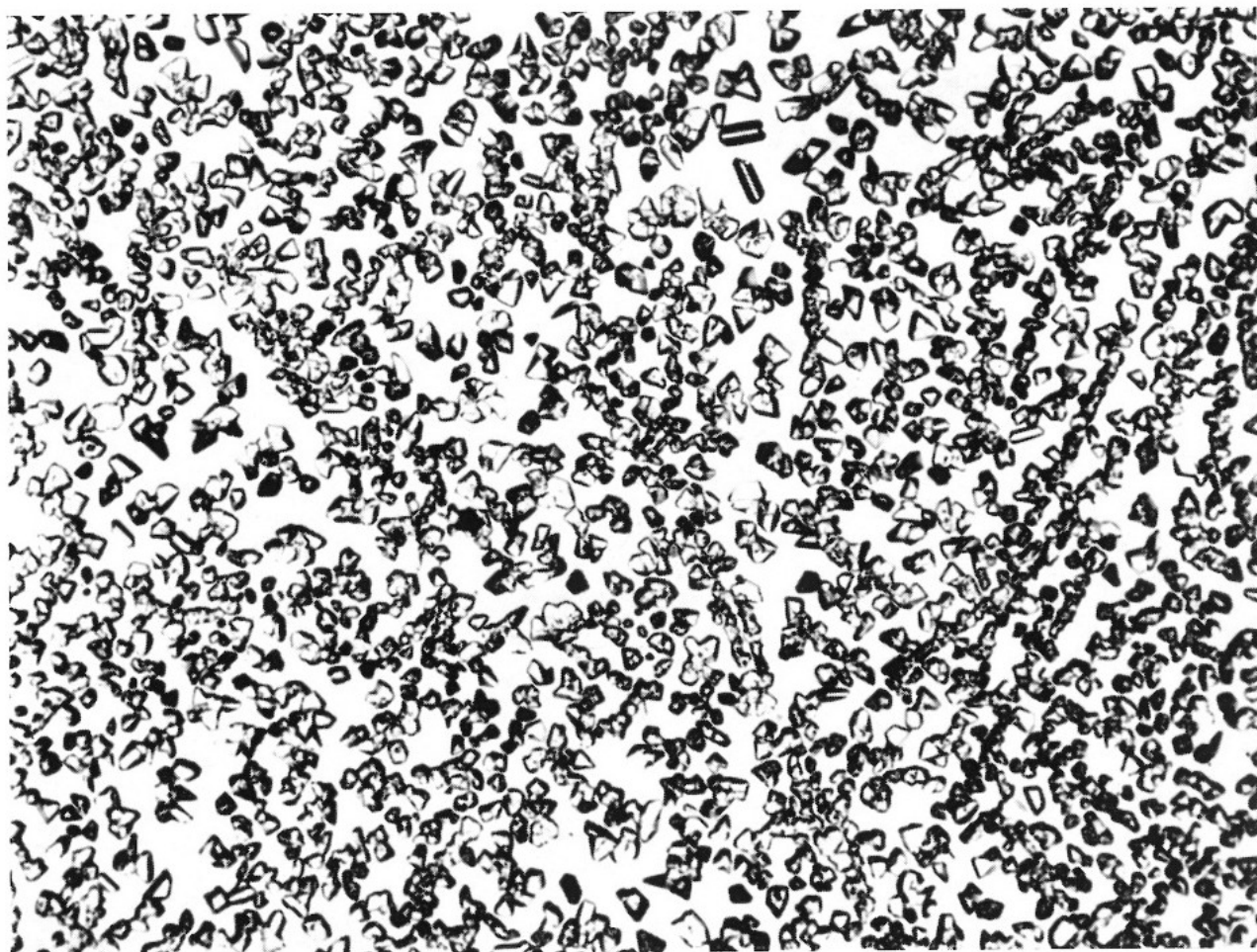


Plate 5. Fig. 8. - As above from 10 % Isodrin.

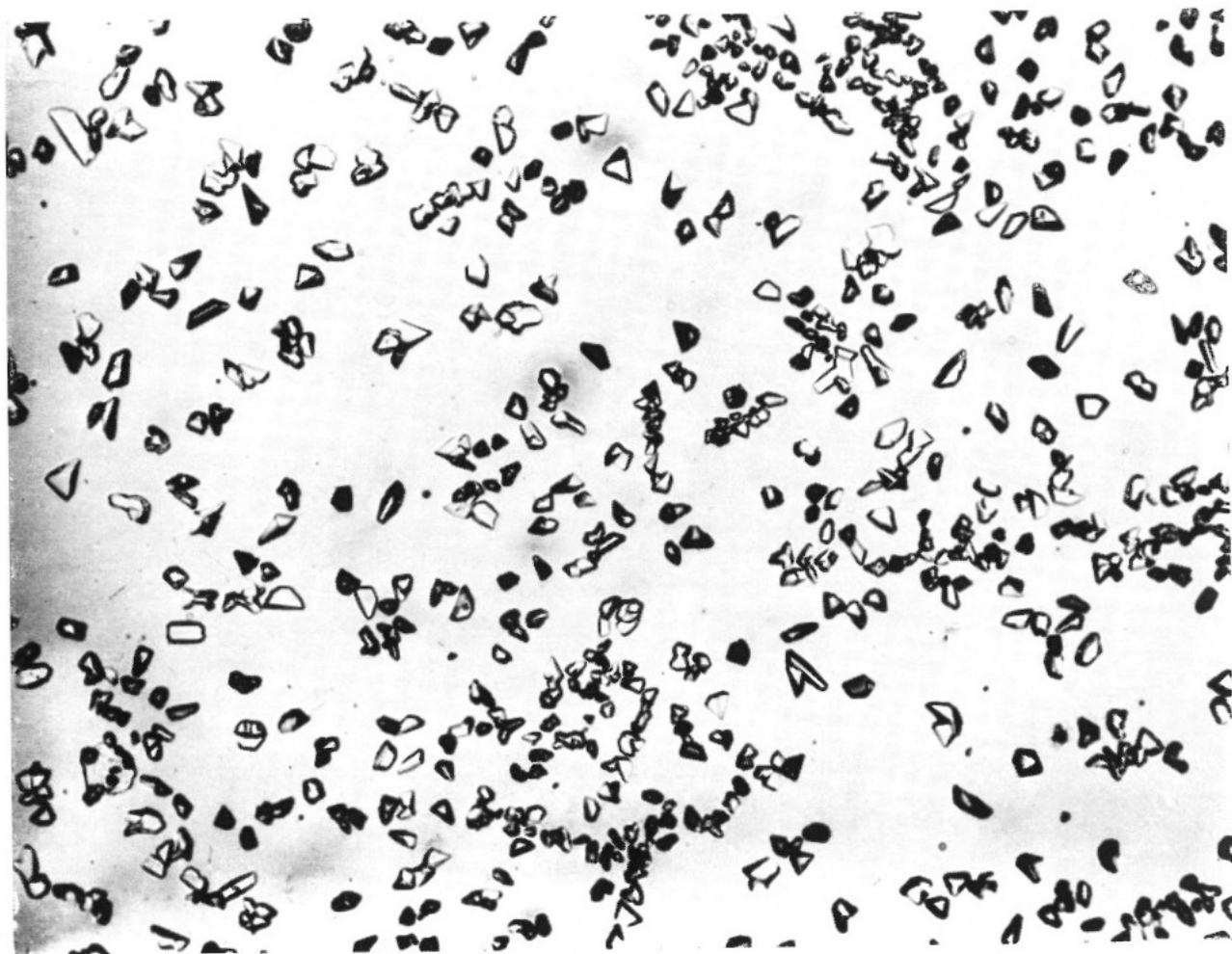


Plate 5. Fig. 9. - As above from 5 % Isodrin.



harder than when plasticized but which were unserviceable for practical purposes because they were brittle and cracked. As, however, there might be special cases where UF coatings with low plasticizer content might be useful and also in order to demonstrate further the influence of hardness on surface blooming of DDT, a range of coatings was prepared varying the proportion of urea to castor oil alkyd resin. (Plate 2. Figs 2, 3, 4). Thirty adults of *Tribolium castaneum* were placed on each coating overnight with the effects as illustrated. The more plasticizer was added the heavier the bloom of crystals. The range of kills of the flour beetles was from 70 per cent for the hardest coating up to 95 per cent for the softest. After ageing for a week all coatings had perceptible blooms of crystals.

It was evident that cleaning operations would result in very different weights of DDT being lost. This would be a factor of some practical importance as affecting the residual life of the coating. So long as insecticidal efficiency were not sacrificed it would be better to use a formulation which was more economical in its release of DDT in response to mechanical stimulation of any kind. EMERY (1949) <sup>(19)</sup> pointed out that only a small number of DDT crystals was necessary to give fairly high kills of insects and GOULD (1948) <sup>(20)</sup> suggested that DDT crystals of smaller size were more toxic to German roaches. As the range of kills of flour beetles from the resin films described above was so short, it gave support to the conclusions of these workers. The illustrations show much smaller size and number of crystals in the blooms of the harder coatings when compared with ratios of Urea/Alkyd of 50/50 and above.

Measurements were made of the relative weight losses of DDT crystals by cleaning with xylol harder and softer coatings twice at intervals after allowing ageing for 20 weeks.

BLOCK suggested that an increased proportion of plasticizer would tend to reduce blooming but it was not possible to demonstrate this, but rather the opposite occurred.

TABLE 5.

*Relative loss of DDT by cleaning from coatings of different hardness.*

| % DDT | Sward Rocker Units | % Loss of Wt. | Age      |
|-------|--------------------|---------------|----------|
| 40    | 28                 | 26            | 20 weeks |
| 20    | 32                 | 17            | 20 weeks |
| 20    | 46                 | 13            | 20 weeks |

## 2) Irradiation by Ultra Violet light.

German Patent Number 416,252 <sup>(21)</sup> stated that UF resins were hardened by exposure to ultra violet light. Tests were made using an Esira Black mercury vapour lamp (with the envelope removed) placed at 14 inches from air-dried coatings on glass plates.

Urea resins are opaque to ultra violet light so that it was not possible to cure UF coatings entirely by this means. A standard lacquer consisting of equal proportions of urea to castor oil alkyd was first air-dried by acid catalyst added in the usual proportion of 1:20 parts of lacquer. It was found that exposure to ultra violet light of coatings containing 20% DDT for quite short periods from a quarter of an hour upwards caused a striking reduction in the tendency to produce blooms of DDT, again with a corresponding fall in toxicity to flies or mosquitoes. Abrasion of the surface resulted in the formation of a bloom and this indicated that the effect of the ultra violet light was confined to the surface of the film.

It is worth noting that ultra violet light did not reduce the toxicity of the DDT itself although this was in solution within the UF coating. This was an important point because it is well established that ultra violet light decomposes DDT on oil solutions.

## 3) Effect of high-boiling solvents on surface crystallization.

The normal solvents for UF coatings are mixtures of xylene and butyl alcohol. Lacquers with these solvents have a flash point of about 78° F. It was considered desirable to have available for special cases lacquers with higher flash points. Accordingly, British Industrial Plastics Ltd. prepared lacquers with flash points of above 90° F using as solvents nonanol or benzyl alcohol to replace butyl alcohol, and solvent 15-9 C (ex Petrochemicals) to replace xylene.

Air-dried coatings containing 20% DDT which were prepared on glass plates and stimulated by contact with *Tribolium* for a contact period of two hours, showed a heavy bloom of DDT within 24 hours. Further, the coatings incorporating benzyl alcohol bloomed spontaneously over the whole surface not exposed to *Tribolium*, while the coating containing nonanol also bloomed spontaneously to some extent.

A range of these coatings was prepared in which the ratio of urea resin to castor oil alkyd was varied as before, but the resulting coatings all bloomed freely, with very little difference in crystal size and number even at 70/30 Urea/Alkyd resin.

It was evident that high-boiling solvents would tend to be lost from air-dried coatings rather more slowly than xylene/butanol, and would therefore keep the coatings softer.

#### BEHAVIOUR OF OTHER INSECTICIDES IN UF COATINGS.

After further experiments had shown that no bloom or insecticidal action could be shown with concentrations of DDT lower than 5% on the resin solids, a number of other insecticides was examined.

Dieldrin, used as a pure recrystallized material or as a technical material containing 95% active ingredient, produced surface crystals similar to those of DDT at 5% concentration and upwards, but to a much less degree than DDT. Toxicity to *Aedes* again varied according to the presence or absence of a bloom.

TABLE 6.

*The toxicity of 20% Dieldrin in urea-formaldehyde resin, before blooming had occurred, to 1-day old Aedes Aegypti*

| Contact time | Number of mosquitoes | Per cent dead after 24 hours | Bloom |
|--------------|----------------------|------------------------------|-------|
| 1 minute     | 92                   | 0                            | Nil   |
| 2 minutes    | 71                   | 40                           | Nil   |
| 4 minutes    | 81                   | 57                           | Nil   |
| 8 minutes    | 79                   | 100                          | Nil   |

After surface crystallization had occurred the toxicity of dieldrin resins improved considerably.

TABLE 7.

*Toxicity of air-dried UF coatings containing Dieldrin to Aedes Aegypti, after surface crystallization.*

| Per Cent Conc. Dieldrin | Contact time | Numbers Aedes used | Per cent kill after 24 hours | Bloom  |
|-------------------------|--------------|--------------------|------------------------------|--------|
| 5                       | 8 minutes    | 143                | 35                           | Poor   |
| 5                       | 16 minutes   | 127                | 96                           | »      |
| 10                      | 4 minutes    | 153                | 18                           | Slight |
| 10                      | 8 minutes    | 143                | 98                           | »      |
| 20                      | 1/2 minute   | 128                | 30                           | Good   |
| 20                      | 1 minute     | 140                | 60                           | »      |
| 20                      | 2 minutes    | 139                | 90                           | »      |
| 20                      | 4 minutes    | 146                | 100                          | »      |

The blooms of crystals referred to in Table 7 were induced by confining *Tribolium* on the coatings for 24 hours. The intensity of bloom (i.e. the numbers and size of crystals) was much less on the 5% Dieldrin coating than the 20% coating.

The potency of the coatings was affected by concentration of insecticide, which also influenced the size and shape of the crystals. The latter is illustrated in Plate 5. Above a certain limit, which was not the same with all compounds, the insecticide tended to bloom spontaneously as very large crystals. Only in the case of aldrin was induced crystallization absent, although spontaneous bloom appeared at 40% concentration. (Plate 4, Fig. 6). Experiments with ultra violet light had shown how DDT could be imprisoned within UF coatings with no degradation of the insecticide. This work led to a consideration of pyrethrum as an insecticide for long lasting residues in UF coatings. The good properties of fast knock-down and low mammalian toxicity of pyrethrum are generally known. Using the standard lacquer containing 50/50 Urea/Alkyd resins a series of air-dried coatings was prepared from 25% pyrethrum concentrate on glass, stored at 25° C, and RH 70% in a dark room and tested after two days.

The data in Table 8 showed that both flies and mosquitoes were affected by the pyrethrum coatings, although there was no crystalline

TABLE 8.

*Knockdown rates of mixtures of pyrethrines and piperonyl butoxide in UF coatings on Aedes and Musca confined under 7 cm petri dishes*

| Insect | Insecticide     | Time for knockdown in minutes |     |
|--------|-----------------|-------------------------------|-----|
|        |                 | 50%                           | 95% |
| Aedes  | 1% Pyrethrines  | 19                            | 35  |
|        | 0.8% Pyr. 8% PB | 19                            | 35  |
|        | 0.6% Pyr. 8% PB | 19                            | 36  |
|        | 0.4% Pyr. 8% PB | 20                            | 41  |
|        | 0.2% Pyr. 8% PB | 20                            | 67  |
| Musca  | 1% Pyrethrines  | ∞                             | ∞   |
|        | 0.8% Pyr. 8% PB | 27                            | 36  |
|        | 0.6% Pyr. 8% PB | 27                            | 36  |
|        | 0.4% Pyr. 8% PB | 35                            | 61  |
|        | 0.2% Pyr. 8% PB | 71                            | 80  |



bloom but a slight greasy exudate. *Aedes* was more affected than *Musca*, which was not affected by pyrethrins alone.

Coatings were prepared containing much higher concentrations of pyrethrum. Above 5% pyrethrum the coatings tended to become rather soft, so that a ratio of 60/40 Urea/Alkyd was necessary for 10% Pyrethrines and 80% piperonyl butoxide on the resin solids.

Using the generally accepted proportion of eight parts of the synergist piperonyl butoxide to one of pyrethrines, tests with *Aedes* showed a slight reduction in effect produced by piperonyl butoxide with very short contact times.

TABLE 9.

*Toxicity of Pyrethrines/Piperonyl butoxide mixture in UF resins to Aedes Aegypti from short contacts*

| % Insecticide | Contact time | Numbers Used | Per Cent Dead after 24 hours |
|---------------|--------------|--------------|------------------------------|
| 5 Pyrethrines | 1 minute     | 21           | 52                           |
| 5 Pyrethrines | 2 minutes    | 24           | 78                           |
| 5 Pyrethrines | 4 minutes    | 26           | 83                           |
| 5 Pyrethrines | 8 minutes    | 18           | 85                           |
| 5 Pyrethrines | 16 minutes   | 18           | 90                           |
| 5 Pyr. 40 PB  | 1 minute     | 30           | 32                           |
| 5 Pyr. 40 PB  | 2 minutes    | 42           | 75                           |
| 5 Pyr. 40 PB  | 4 minutes    | 35           | 95                           |
| 5 Pyr. 40 PB  | 8 minutes    | 41           | 96                           |
| 5 Pyr. 40 PB  | 16 minutes   | 34           | 96                           |

Experiments were then made to determine the residual life of pyrethrum formulations under different storage conditions. A lacquer containing 5% Pyrethrines 40% Piperonyl butoxide was painted on to sets of 4 x 4 inch plywood plaques previously coated with a flat primer paint. Representative plaques were hung in early October on an external south wall, a north wall, on the laboratory wall facing the window and on the wall of a constant temperature room lighted by electricity only. Before weathering all coatings showed a high and equal toxicity to *Aedes*. In table 10 data are presented on the subsequent fall in potencies associated with the different conditions of weathering.

Weathering out-of-doors in full sunlight as on a south wall had

the most destructive effects on the pyrethrum, while storage on the north wall had noticeably less effect. Indoors, there was little difference caused by keeping the coatings at normal room conditions or in a constant temperature.

Similar coatings on unpainted metal and glass surfaces had a much longer residual action, and it seemed evident that the toxicity of these pyrethrum coatings might be adversely affected by an absorbent surface, whether this was a priming paint or a soft wood. A similar coating applied to brown paper which was then stored at room temperature within folder covers retained its knockdown toxicity to *Aedes* unimpaired for 22 weeks. A harder coating containing 10% pyrethrum and 80% piperonyl butoxide applied to copper mesh mosquito netting and subsequently stored on the laboratory bench for 26 weeks also gave 95% knockdown within 12 minutes followed by 100% kill after 24 hours.

TABLE 10.

*Effect of storage conditions on the residual toxicity to Aedes of pyrethrum in UF coatings*

| Storage    | Contact time<br>in minutes | Average per cent kill after 24 hours |    |
|------------|----------------------------|--------------------------------------|----|
|            |                            | Coating age in days<br>18            | 24 |
| South wall | 64                         | 13                                   | —  |
|            | 128                        | 41                                   | 3  |
| North wall | 64                         | 76                                   | 30 |
|            | 128                        | 100                                  | 70 |
| Laboratory | 1                          | 10                                   | —  |
|            | 2                          | 68                                   | 0  |
|            | 8                          | —                                    | 31 |
|            | 16                         | 93                                   | 43 |
| CT Room    | 2                          | 90                                   | 10 |
|            | 4                          | 95                                   | 17 |
|            | 8                          | —                                    | 33 |

Tests were made with pyrethrum coatings against a strain of flies from Sardinia resistant to DDT and other chlorinated hydrocarbons.

The tests with Sardinian flies showed that these were very resistant to pyrethrum coatings stored indoors, although they were knocked

down when confined on the coatings under petri dishes. The addition of a volatile insecticide like BHC had a marked effect not only in causing a very fast knockdown but also in giving complete kills. In Table 11 the flies were allowed to remain on the «BHC» coating for 60 minutes, as were the flies on the coating containing 5% Pyrethrum 40% piperonyl butoxide. HEWLETT <sup>(22)</sup> has observed that BHC appeared to increase the toxic effects of pyrethrum to *Calandra*. Coatings containing pyrethrum, piperonyl butoxide and BHC might be effective under practical conditions against resistant houseflies.

TABLE 11.

*Toxicity of pyrethrum in UF coatings of different ages to a strain of resistant flies*

| Insecticide           | Surface     | Coating age | Knockdown in minutes |      | Per cent kill after 24 hours |
|-----------------------|-------------|-------------|----------------------|------|------------------------------|
|                       |             |             | 50 %                 | 95 % |                              |
| 5% Pyr. 40% PB        | Fibre-board | 16 weeks    | 20                   | 25   | 0                            |
| 10%Pyr. 80% PB        | Wood        | 8 weeks     | 11                   | 15   | 0                            |
| 5% Pyr. 40% PB 5% BHC | Glass       | 3 weeks     | 3                    | 5    | 100                          |

Gamma BHC and Aldrin are both compounds with fairly high vapour pressure. In air-dried coatings Aldrin produced large amorphous crystals spontaneously at 40% concentration (Plate 4, Fig. 6) but crystals could not be induced by surface stimulation which did occur with 20% gamma BHC.

One of the most important differences between the toxicities of volatile materials like BHC and Aldrin and non-volatile materials like DDT and Dieldrin rested in the fact that volatile compounds exerted their maximum toxicity on fresh coatings irrespective of whether surface crystallization had occurred or not. There was therefore a progressive fall in the toxicity of BHC and Aldrin coatings with age. This toxicity was due to the vapour emerging from the solid solution of insecticide held below the surface of the coating.

Tests in which coatings containing BHC or Aldrin were scrubbed in warm water and detergent showed no significant difference in toxicity immediately before or after cleaning. This phenomenon provided an answer to the problem postulated by HARRISON who suggested that insecticidal flat-oil paints containing DDT be wiped down in order to induce the blooming necessary to give high toxicity to flies. The use

of volatile insecticides would make such actions unnecessary. It will be appreciated that volatile compounds would continue to expend themselves irrespective of cleaning operations and would tend to have shorter residual action than non-volatile insecticides.

Air-dried films on glass plates using Aldrin which were stored at room temperature remained toxic for periods which were longer with the heavier quantities of Aldrin used.

TABLE 12.

*Residual toxicities of Aldrin in UF coatings to Aedes aegypti by contact action*

| Per Cent Aldrin | Age in Aldrin | Average % kill after 24 hours contact time in minutes |    |     |     |     |     |     |
|-----------------|---------------|-------------------------------------------------------|----|-----|-----|-----|-----|-----|
|                 |               | 1/2                                                   | 1  | 2   | 4   | 8   | 16  | 32  |
| 5               | 1             | 0                                                     | 0  | 5   | 49  | 75  | 100 | 100 |
| 10              | 1             | 0                                                     | 10 | 30  | 75  | 100 | 100 | 100 |
| 20              | 1             | 10                                                    | 66 | 75  | 100 | 100 | 100 | 100 |
| 40              | 1             | 10                                                    | 75 | 100 | 100 | 100 | 100 | 100 |
| 5               | 12            | 0                                                     | 0  | 0   | 0   | 0   | 0   | 0   |
| 10              | 12            | 0                                                     | 0  | 0   | 0   | 30  | 95  | 100 |
| 20              | 12            | 0                                                     | 0  | 0   | 5   | 95  | 100 | 100 |
| 40              | 12            | 5                                                     | 36 | 95  | 100 | 100 | 100 | 100 |

Tests on the vapour toxicity of Aldrin in these air-dried coatings showed a lasting residual action which increased with the weight of insecticide incorporated into the coatings.

Gamma BHC, used as 90% pure compound or as «Lindane» in order to avoid the unpleasant musty odour of the delta and other

TABLE 13.

*Residual vapour toxicity of Aldrin in UF coatings on glass to Musca*

| Per cent Aldrin | Exposure time in minutes necessary for 75% kill |    |    |     |
|-----------------|-------------------------------------------------|----|----|-----|
|                 | Age of deposit in weeks                         |    |    |     |
|                 | 1                                               | 4  | 8  | 12  |
| 5               | 60                                              | 60 | 90 | 120 |
| 10              | 30                                              | 45 | 60 | 90  |
| 20              | 20                                              | 20 | 20 | 30  |
| 40              | 20                                              | 20 | 20 | 30  |



isomers, gave similar results for residual action against flies and mosquitoes.

Weathering and other physical conditions would necessarily have effects on the residual action of volatile insecticides. Even 20% gamma in an air-dried coating was found to be non-toxic to *Aedes* when hung on a south wall after three summer months. At the end of that time both 20% DDT and 20% Dieldrin maintained the same high level of toxicity to *Aedes*. Similar results were obtained in field trials against barnacles (BRACY, 1953; WAUGH, et al., 1952).

By differentially hardening the surface of air-dried UF coatings by exposure to ultra-violet irradiation, it was possible to slow down the rate of loss by evaporation of Aldrin and BHC.

TABLE 14.

*Effect of ultra violet irradiation on the contact toxicity to Musca of UF coatings containing BHC or Aldrin*

| Age of Coating | Insecticide | Ultra violet irradiation | 95% knockdown of Musca after minutes |
|----------------|-------------|--------------------------|--------------------------------------|
| 7 days         | 5% BHC      | 0 hours                  | 30                                   |
| 7 days         | 5% BHC      | 2 hours                  | 340                                  |
| 7 days         | 5% BHC      | 4 hours                  | 440                                  |
| 7 days         | 5% Aldrin   | 0 hours                  | 170                                  |
| 7 days         | 5% Aldrin   | 2 hours                  | 450                                  |
| 7 days         | 5% Aldrin   | 4 hours                  | > 450                                |

After ageing for a further seven days all the coatings were sand-papered lightly to remove the hardened «skin» of resin and then washed in tap-water and detergent to remove all debris. Houseflies were then confined directly on the coatings under perspex rings enclosed by copper gauze. The results, given below, reflect the increased rate of evaporation in the greater kills obtained.

TABLE 15.

*Effect of sand-papering older UF coatings irradiated by ultra violet light on toxicity to Musca*

| Age of Coating | Insecticide | Ultra violet irradiation | 95% knockdown of Musca after minutes |
|----------------|-------------|--------------------------|--------------------------------------|
| 14 days        | 5% BHC      | 0                        | 25                                   |
| 14 days        | 5% BHC      | 2                        | 25                                   |
| 14 days        | 5% BHC      | 4                        | 35                                   |
| 14 days        | 5% Aldrin   | 0                        | 15                                   |
| 14 days        | 5% Aldrin   | 2                        | 160                                  |
| 14 days        | 5% Aldrin   | 4                        | 170                                  |

Tests were made to check the effect of temperature on the toxicity of several volatile insecticides in air-dried coatings, stored at room temperature.

TABLE 16.

*The effect of temperature on the rate of knockdown of houseflies by some insecticides in UF coatings*

| Testing Temperature | Insecticide | Surface          | Coating Age in weeks | Knockdown in Minutes |     | Bloom |
|---------------------|-------------|------------------|----------------------|----------------------|-----|-------|
|                     |             |                  |                      | 50%                  | 95% |       |
| 18°C                | 5% Aldrin   | Glass            | 28                   | 145                  | 165 | Nil   |
| 25°C                | 5% Aldrin   | Glass            | »                    | 105                  | 118 |       |
| 18°C                | 5% Isodrin  | Glass            | 10                   | 145                  | 165 | Nil   |
| 25°C                | 5% Isodrin  | Glass            | »                    | 90                   | 95  |       |
| 18°C                | 5% BHC      | Glass            | 25                   | 70                   | 85  | Nil   |
| 25°C                | 5% BHC      | Glass            | »                    | 55                   | 65  |       |
| 18°C                | 10% BHC     | East African mud | 51                   | 70                   | 90  | Nil   |
| 25°C                | 10% BHC     | East African mud | »                    | 70                   | 80  |       |

The flies were confined under petri dishes and so the results may have little significance for practical purposes, except in indicating that at higher temperature more vapour was given off with a consequent faster knockdown. All coatings were washed with water immediately before the tests. BHC showed much faster knockdown than Aldrin or Isodrin, and also much less difference in effect at the higher and lower temperatures.

TABLE 17.

*The effect of higher proportions of Urea resin to plasticizer on the toxicity of BHC in UF coatings to Musca*

| % BHC | Ratio of Urea to Alkyd resin | Coating age in weeks | Treatment   | 95% Knockdown in Minutes |
|-------|------------------------------|----------------------|-------------|--------------------------|
| 5     | 25/75                        | 7                    | None        | 25                       |
| 5     | 50/50                        | 7                    | None        | 30                       |
| 5     | 75/25                        | 7                    | None        | 113                      |
| 5     | 25/75                        | 7                    | Sandpapered | 23                       |
| 5     | 50/50                        | 7                    | Sandpapered | 23                       |
| 5     | 75/25                        | 7                    | Sandpapered | 22                       |

Some effect on the rate of evaporation of BHC could also be made by using higher proportions of urea to alkyd resin, although such coatings might not be of great durability under practical conditions. All coatings were washed in soapy water immediately before testing and again after sandpapering.

A notable difference between volatile and non-volatile insecticides was the much lower concentrations at which the former were toxic to insects. Below 5% concentration on the weight of resin solids DDT failed to bloom and was non-toxic, but both BHC and Aldrin were toxic to *Musca* at concentrations as low as 0.25% on the resin solids in fresh coatings. The residual life of such coatings was naturally very short and had ceased after five weeks in the laboratory.

Isodrin is a volatile insecticide which bloomed readily in air-dried UF coatings, and showed a range of form and size of crystal according to the concentration. (Plate 5, Figs 7, 8, 9).

Surface-hardening having been shown to influence the rate at which toxic vapours left UF coatings, experiments were made to determine whether such vapours could be released by the incorporation of non-insecticidal compounds with very large molecules. FINN and LEWIS (1951) (<sup>23</sup>) had shown that the water permeability of phenol formaldehyde resin coatings was reduced by harder curing and suggested that molecules of different sizes might be screened by differential hardening of such coatings.

TABLE 18.

*Effect of molecule shape on the vapour toxicity to Musca of Isodrin and Aldrin in irradiated UF coatings previously air-dried with a catalyst.*

| Coating Age | Insecticide | Ultra violet irradiation in hours | Knockdown Rate in Minutes |     | Per cent kill after 24 hours |
|-------------|-------------|-----------------------------------|---------------------------|-----|------------------------------|
|             |             |                                   | 50%                       | 95% |                              |
| 2 days      | 5% Aldrin   | 0                                 | 220                       | 270 | 100                          |
|             | » »         | 1/4                               | 270                       | 270 | 100                          |
|             | » »         | 1/2                               | 270                       | 270 | 29                           |
|             | » »         | 1                                 | 270                       | 270 | 25                           |
|             | 5% Isodrin  | 0                                 | 270                       | 270 | 100                          |
|             | » »         | 1/4                               | 270                       | 270 | 25                           |
|             | » »         | 1/2                               | 270                       | 270 | 20                           |
|             | » »         | 1                                 | 270                       | 270 | 20                           |

Experiments were made with volatile insecticides by exposing insects in the apparatus described above to the vapours arising from UF coatings.

Isodrin is a stereoisomer of Aldrin, the latter being the endo-isomer with a molecule not so big spatially as Isodrin. It would be expected therefore that a differentially hardened surface of a UF coating would be likely to seal in Isodrin more effectively than Aldrin.

The data show how ultra violet irradiation even for 15 minutes had a much more marked effect in reducing the toxicity of Isodrin than Aldrin.

Similar air-dried coatings containing 50/50 Urea/Alkyd resins were then tested with a non-insecticidal compound of very large molecule size. Alphahydroxy alpha methyl butyric acid has been used by LOVELOCK <sup>(24)</sup> for experiments in air disinfection, and recognized as having bactericidal action of a fairly high order.

Large molecules might be expected to have some effect on the apparent toxicity of volatile insecticides in UF coatings, by preventing the formation of a closely polymerized surface. Recrystallized Bieldrin and DDT were used in comparative trials with «C» acid.

The data in *Table 19* summarizes some results obtained with combinations of 2% Aldrin or 2% BHC with «C» acid, Dieldrin or DDT. The kills are comparative within the different groups but not strictly from group to group because they were obtained with different insect cultures.

It is apparent that although DDT, Dieldrin and «C» acid caused no kills in the vapour phase when used alone, they all had the effect of increasing the toxicity of BHC and Aldrin to some extent. This might be described as a form of physical synergism analogous to that for anti-mosquito sprays described by DAVID and BRACEY (1944) <sup>(25)</sup>. BHC was influenced much less than Aldrin, and the non-insecticidal «C» acid, with the largest molecule, was the most effective of all the compounds tested.

The precise cause of this physical activation is not fully understood but it may be due to a combination of effects on the UF coating surface as well as to a simple «crowding» effect on the molecules of vapour. A relatively smaller molecule like BHC would thus be less likely to be affected than the molecule of Aldrin. Volatile insecticides with large molecules could thus be made more available on the surface of UF coatings by the inclusion of compounds having very much bigger molecules. It also offers a possible means of ensuring that all the insecticide is used and none left behind in the coating. A curious feature



was the apparent « synergism » between DDT and Aldrin and *Musca* which was not present with Aldrin and Dieldrin mixtures.

#### THE EFFECT OF SURFACES ON THE TOXICITY OF UF COATINGS.

The literature on insecticidal residues contains many references to the influence exerted by different surfaces on the insecticidal potencies of residues under practical conditions. Insecticides may be lost from the surface by absorption of solutions or adsorption of vapours on to wood, soils, textiles, or paint.

Some experiments were carried out to compare the effectiveness of standard insecticidal residues with the UF resins when using some of the testing techniques employed in this investigation. The type of surface was found to have an overriding influence on the toxicity of these residues.

Some data in Table 20 suggest the degree of variability in the toxicity to *Aedes* of equivalent weights of DDT residues on different surfaces.

TABLE 19.

*The vapour toxicity to Aedes and Musca of Aldrin and BHC when mixed with non-volatile compounds in UF coatings*

| Coating age in days | % Insecticide       | Insect | Exposure time in hours | Per Cent kill after 24 hours | Bloom   |
|---------------------|---------------------|--------|------------------------|------------------------------|---------|
| 12                  | 2 BHC               | Musca  | 2                      | 12                           | Absent  |
| 12                  | 2 BHC/20 Dieldrin   | Musca  | 2                      | 22                           | Present |
| 12                  | 2 BHC/20 « C » acid | Musca  | 2                      | 27                           | Absent  |
| 12                  | 2 BHC               | Aedes  | 1.5                    | 100                          | Absent  |
| 12                  | 2 BHC/20 Dieldrin   | Aedes  | 1.5                    | 100                          | Present |
| 12                  | 2 BHC/20 « C » acid | Aedes  | 1.5                    | 100                          | Absent  |
| 12                  | 2 Aldrin            | Musca  | 2                      | 18                           | Absent  |
| 12                  | 2 Ald/20 Dieldrin   | Musca  | 2                      | 14                           | Present |
| 12                  | 2 Ald/20 « C » acid | Musca  | 2                      | 63                           | Absent  |
| 6                   | 2 Aldrin            | Musca  | 3                      | 27                           | Absent  |
| 6                   | 2 Ald/20 Dieldrin   | Musca  | 3                      | 24                           | Present |
| 6                   | 2 Ald/20 « C » acid | Musca  | 3                      | 73                           | Absent  |
| 6                   | 2 Ald/20 DDT        | Musca  | 3                      | 52                           | Present |
| 6                   | 2 Aldrin            | Aedes  | 1.5                    | 12                           | Absent  |
| 6                   | 2 Ald/20 Dieldrin   | Aedes  | 1.5                    | 13                           | Present |
| 6                   | 2 Ald/20 « C » acid | Aedes  | 1.5                    | 52                           | Absent  |
| 6                   | 2 Ald/20 DDT        | Aedes  | 1.5                    | 4                            | Present |
| 6                   | 20 Dieldrin         | Musca  | 3                      | 2                            | Present |
| 6                   | 20 DDT              | Musca  | 3                      | 0                            | Present |
| 6                   | 20 « C » acid       | Musca  | 3                      | 0                            | Absent  |

N. B. - « C » acid = alpha hydroxy alpha methyl butyric acid.

TABLE 20.  
Some comparative toxicities of DDT residues to *Aedes aegypti*

| Insecticide                                                | Residue type        | Dosage<br>mg/sq. ft | Surface                                                                                             | Average % kill after 24 hours Contact time in Minutes |     |     |     |     |     |     |    |     |  |
|------------------------------------------------------------|---------------------|---------------------|-----------------------------------------------------------------------------------------------------|-------------------------------------------------------|-----|-----|-----|-----|-----|-----|----|-----|--|
|                                                            |                     |                     |                                                                                                     | 1/4                                                   | 1/2 | 1   | 2   | 4   | 8   | 16  | 32 | 64  |  |
| DDT paste<br>without Teepol<br>DDT paste with<br>5% Teepol | Water<br>suspension | 100                 | Fibreboard                                                                                          |                                                       |     |     | 8   | 10  | 68  |     |    |     |  |
|                                                            |                     | 100                 | Fibreboard                                                                                          |                                                       |     |     | 54  | 81  | 98  |     |    |     |  |
| DDT xylene<br>emulsion                                     | Emulsion            | 100                 | Glass                                                                                               | 0                                                     | 0   | 0   | 0   | 0   | 5   | 5   |    | 100 |  |
|                                                            |                     | 100                 | Plywood                                                                                             |                                                       |     | 26  | 50  | 95  | 100 |     |    |     |  |
|                                                            |                     | 100                 | Unpainted softwood                                                                                  |                                                       |     | 65  | 100 | 100 |     |     |    |     |  |
|                                                            |                     | 100                 | Fibreboard                                                                                          |                                                       |     | 48  | 70  | 100 |     |     |    |     |  |
| DDT xylene<br>emulsion plus<br>40% High<br>Boiling Oil     | Emulsion            | 100                 | Glass                                                                                               | 10                                                    | 30  | 60  | 85  |     |     |     |    |     |  |
|                                                            |                     | 100                 | Plywood                                                                                             |                                                       |     |     | 0   | 0   | 5   | 60  |    |     |  |
|                                                            |                     | 100                 | Fibreboard                                                                                          |                                                       |     |     | 0   | 0   | 5   |     |    |     |  |
| DDT xylene<br>emulsion plus<br>50% Phosphate               | Emulsion            | 100                 | Glass                                                                                               | 80                                                    | 98  | 100 | 100 |     |     |     |    |     |  |
|                                                            |                     | 100                 | Plywood                                                                                             |                                                       |     |     |     |     | 0   | 5   | 30 |     |  |
|                                                            |                     | 100                 | Fibreboard                                                                                          |                                                       |     |     |     |     |     |     |    |     |  |
| 20% DDT on<br>UF resin<br>solids                           | UF coating          |                     | Glass<br>Tinplate<br>Plywood<br>Fibreboard<br>Mud<br>Paper<br>Fresh flat<br>primer paint<br>on wood |                                                       |     |     |     |     |     |     |    |     |  |
|                                                            |                     | 630                 | Fresh high-gloss paint                                                                              |                                                       |     |     | 0   | 60  | 95  | 100 |    |     |  |
|                                                            |                     | 630                 |                                                                                                     |                                                       |     |     |     |     |     | 0   | 30 | 40  |  |

It would be more accurate to ascribe the different toxicities to the interaction between the formulation and the surface. The DDT paste (DE DE TANE) consisted of microcrystals approximately six microns by one micron in sulphite lyes which would cause the crystals to remain somewhat tacky and therefore adhere to the surface. The addition of the wetting agent Teepol « washed » the crystals and left them lying more freely available to *Aedes* on the absorbent fibre board, into which the solution of lyes, Teepol and water was absorbed.

The toxicities of xylene emulsion on various surfaces varied considerably. On glass the liquid phase evaporated to leave flat crystals of DDT strongly adherent to the glass. On the plywood, softwood and fibreboard a bloom of DDT crystals appeared within four days, with a much higher toxicity to the mosquitoes.

Addition of high boiling lube oil or phosphate ester, while leaving a wet and highly toxic oily residue on glass prevented the formation of a bloom from the absorbent wood and fibreboard.

Urea formaldehyde resin coatings provided their « own » surfaces on various absorbent and non-absorbent surfaces alike, from which the DDT bloomed in the manner described. On fresh high gloss oil paints, however, the resin lacquer was of very poor toxicity and this was associated with a failure to produce a bloom of crystals.

Although UF coatings are normally applied direct to wood or other surfaces, and only infrequently over even a priming paint, it is as well to appreciate that coatings for insecticidal purposes would not be satisfactory when applied to high gloss or similar finishes.

#### BIOLOGICAL FACTORS AFFECTING THE POTENCY OF UF COATINGS.

##### 1) *Repellency of Insecticides.*

GILMOUR and KENNEDY observed that DDT residues repelled houseflies and mosquitoes. With non-volatile insecticides at least, therefore, such a factor would be likely, as KENNEDY indicated, to prevent the efficient destruction of insects by causing the pick-up of only sub-lethal dosages. This could be a very serious matter affecting the efficiency of long-lasting residues from semi-permanent UF coatings. Sub-lethal contacts would be likely to encourage the development of resistant strains of flies and mosquitoes.

The proper assessment of repellency in terms which would be of practical significance is an exceedingly complex problem. It is certain that different species will not react in the same way to the same or

different compounds. In some tests <sup>(18)</sup> with *Glossina palpalis*, used individually, the results with the same coatings varied according to details of procedure. For example, copper mesh mosquito netting was coated with UF containing 10% pyrethrines 80% piperonyl butoxide (using 60/40 Urea/Alkyd resin), and tests for repellency carried out at 25° C and 70% R.H. gave very different results according to the site of the copper mesh and the pre-conditioning of the tsetse flies.

With the mesh placed on a glass-topped bench the flies remained on an average for 12 seconds (range 8-20 seconds) before flying off. Flies which were first allowed to probe one's arm and then placed on the mesh resting on the other arm, remained for an average of 60 seconds before leaving without probing or feeding; paralysis followed within two minutes and death within 24 hours.

These two cases exemplify some of the factors which may obscure the picture in studies on repellency. Other factors have been considered by DETHIER <sup>(26)</sup> and other workers. Some data on insecticide repellency are quoted in *Table 21*, using tsetses as test insects. In these tests single flies were imprisoned in 6 × 1 inch test tubes in lots of 20. The test surface was strapped as an armlet to the fleshy part of the right forearm. A test-tube was then taken up and the fly shaken lightly on to the left forearm. If no feeding response was shown by lowering of the proboscis the fly was rejected. The fly making a positive response was shaken back into the tube and then transferred to the test surface on the right arm. Each fly made only one contact with the test surface. All the insecticides killed the flies but only pyrethrum prevented feeding. The resting times were longest for DDT, which obviously caused some irritation as evidenced by a frequent changing of position while feeding. Whereas DDT and Dieldrin were present as a bloom of crystals,  $\gamma$  BHC was not. 5% BHC and 20% Dieldrin appeared not to repel *Glossina*.

Observations with *Aedes* in experiments of a different nature, with UF coatings placed inside a cage, showed that when landings were made on bloomed DDT coatings, the mosquitoes left again almost immediately after with no lethal effects.

*Aedes* appeared not to be repelled by coatings containing 10% BHC or 10% Aldrin and remained voluntarily long enough to pick up a fatal dose. But on these two coatings, the mosquitoes would be in contact with the vapour only.

The very high cost of the pyrethrum coatings would rule them out for ordinary practical applications but there might be some use for them in the manner described by PIMENTAL et al. <sup>(27)</sup>, where narrow



TABLE 21.

*Repellency of certain insecticides in UF coatings to Glossina palpalis*

| <i>Insecticide</i> | <i>Coating Age</i> | <i>Surface</i> | <i>Average Contact time</i> | <i>Feeding Response</i> | <i>% Kill after 24 hours</i> |
|--------------------|--------------------|----------------|-----------------------------|-------------------------|------------------------------|
| 10% Pyr. 80% PB    | 10 days            | Copper mesh    | 1 minute                    | Negative                | 100                          |
| 5% DDT on cloth    | 10 days            | Muslin         | 5 minutes<br>(2 to 14 min.) | Positive<br>Replete     | 100                          |
| 5% BHC on cloth    | 10 days            | Muslin         | 3 minutes                   | Positive<br>Replete     | 100                          |
| 20% Dieldrin       | 10 days            | Copper mesh    | 3 minutes                   | Positive<br>Replete     | 100                          |
| 10% Allethrin      | 7 days             | Copper mesh    | 3 minutes                   | Positive<br>No feeding  | 100                          |
| 20% Allethrin      | 7 days             | Copper mesh    | 1 to 1.5 min.               | Positive<br>No feeding  | 100                          |
| Control            | —                  | Copper mesh    | 2-3 minutes                 | Positive<br>Replete     | 0                            |

strips of coated paper or mesh might be tacked to the ceilings of barns or dairies. In such shaded situations the pyrethrum coatings could be expected to last for at least one fly season.

*Musca* prefers to rest on narrow vertical surfaces and it is possible that the use of much lower concentrations of pyrethrum in UF coatings would be effective in keeping dairies free of flies, single contacts serving to drive them out of the building without killing them. Field trials would be necessary to evaluate such considerations.

## 2) *Specific toxicity of insecticides in UF coatings.*

It is well-established that different species of insects vary in their susceptibility to insecticides. In the present investigations examples of such variability were encountered.

On pyrethrum coatings *Aedes* rarely recovered after onset of paralysis, while *Musca* frequently did so, with concentration of 5% pyrethrines on the resin solids.

Some unexpected differences were disclosed by tests of the vapour toxicities of Aldrin and  $\gamma$  BHC to *Aedes* and *Musca*, in which the insects were held one inch away from the coatings.

Tests were made with deposits of  $\gamma$  BHC and Aldrin on filter papers in order to ensure that the specific toxicity was not caused by the UF coatings. The results confirmed the conclusions drawn from the experiments with UF coatings.

TABLE 22.

*Specific toxicities of BHC and Aldrin vapours from UF coatings to Musca and Aedes*

| Test Insect | Insecticide | Coating Age | Average % Kill after 24 hours<br>Exposure time in hours |     |     |     |
|-------------|-------------|-------------|---------------------------------------------------------|-----|-----|-----|
|             |             |             | 1/4                                                     | 1/2 | 1   | 2   |
| Musca       | 10% Aldrin  | 1 day       |                                                         | 65  | 98  |     |
|             | 10% BHC     | 1 day       |                                                         | 6   | 80  |     |
|             | 10% Aldrin  | 10 weeks    |                                                         |     | 40  | 95  |
|             | 10% BHC     | 10 weeks    |                                                         |     | 10  | 46  |
| Aedes       | 10% Aldrin  | 2 days      | 0                                                       | 23  | 84  | 100 |
|             | 10% BHC     | 2 days      | 9                                                       | 90  | 100 | 100 |

The data in Table 19 also indicate specific toxicity of Aldrin/« C » acid mixtures to *Musca* and *Aedes*. Again, Aldrin/DDT mixtures showed a marked increase in the vapour phase toxicity to *Musca* in contrast to that shown against *Aedes*. This might be of practical significance in increasing the potency of UF coatings containing Aldrin against house-flies. Combinations of Aldrin with « C » acid showed marked superiority in toxicity to *Aedes* than combinations of Ald/Dieldrin or Aldrin/DDT. It must be emphasized that these data refer only to the vapour toxicities.

#### THE APPLICATION OF LABORATORY RESULTS TO INDUSTRIAL MANUFACTURING TECHNIQUES

Having evaluated some of the factors which might affect the biological activity of urea formaldehyde coatings whose formulation

TABLE 23.

*Relative toxicities to Musca of Aldrin and BHC vapour from deposits on filter papers*

| Insecticides | Dosage<br>mgm sq.ft | Average % Kill after 24 hours<br>Exposure time in hours |     |     |     |
|--------------|---------------------|---------------------------------------------------------|-----|-----|-----|
|              |                     | 1/4                                                     | 1/2 | 1   | 18  |
| Aldrin       | 25                  | 3                                                       | 47  | 55  | 100 |
| BHC          | 25                  | 0                                                       | 6   | 3   | 100 |
| Aldrin       | 100                 | —                                                       | —   | 100 | —   |
| BHC          | 100                 | —                                                       | —   | 39  | —   |

was based on the practical experience of the resin manufacture, attention was then turned to seeing how the manufacture of insecticidal formulations might fit into existing industrial techniques of handling coatings. This was necessary in order to determine whether such industrial techniques would permit the handling of the lacquers without requiring major adjustments. One of the advantages of urea resins for pesticidal coatings is their wide acceptance in industry for their resistance to mechanical or chemical damage.

#### 1) Paper Coatings.

UF formulations were tested by a firm specializing in the manufacture of paper coatings of all types. Using a curing temperature of 120° F plus 2% of AG. 54 added to the lacquer, rolls of paper were coated in a machine with insecticidal UF lacquers. The handle and other qualities of the paper were satisfactory while permitting the machines to be run at normal speeds. The coated papers were then subjected to insecticidal tests. In between tests the sample papers (four inches wide) were stored at room temperature in loose-leaf covers.

TABLE 24.

*Toxicities to Aedes of UF coatings applied by machine to Kraft paper.*

| <i>Insecticide</i> | <i>Coating type</i> | <i>Age</i> | <i>95% Knockdown<br/>after minutes</i> |
|--------------------|---------------------|------------|----------------------------------------|
| 5% Pyr. 40% PB     | Hard                | 2 days     | 10                                     |
| 5% Pyr. 40% PB     | Hard                | 20 weeks   | 11                                     |
| 5% Pyr. 40% PB     | Soft                | 2 days     | 14                                     |
| 5% Pyr. 40% PB     | Soft                | 20 weeks   | 17                                     |
| 5% BHC             | Hard                | 2 days     | 13                                     |
| 5% BHC             | Hard                | 20 weeks   | 30                                     |
| 5% BHC             | Soft                | 2 days     | 10                                     |
| 5% BHC             | Soft                | 20 weeks   | 16                                     |

Lacquers of two types were used, a « hard » one containing urea and alkyd resins in the proportion of 50/50, and a softer one at 25/75. The liquid pyrethrum insecticides tended to offset the hardening effects of the higher proportions of urea resins. BHC did, however, reflect the greater hardening of the coatings by a slower rate of knockdown by the fresh and old coatings.

A number of tests were made with varying concentrations of DDT in order to find good paper coatings which would be highly insecticidal as well as acceptable in appearance and in other features. The higher concentrations of DDT generally caused an unsightly appearance from a very heavy bloom. Most attention was therefore given to 5% and 10% DDT. The toxicity tests quoted in Table 25 refer to coatings applied to book-cloth but are applicable to KRAFT or other papers.

TABLE 25.

*Toxicity to Aedes of book-cloth mechanically coated with UF lacquers*

| Coating type | % DDT | % Kill after 24 hours<br>Contact time in Minutes |     |    |    | Bloom by naked eye |
|--------------|-------|--------------------------------------------------|-----|----|----|--------------------|
|              |       | 4                                                | 8   | 16 | 32 |                    |
| Hard         | 5     | 16                                               | 28  | 36 | 65 | Nil                |
| Soft         | 5     | 87                                               | 100 | —  | —  | Nil                |
| Hard         | 10    | 15                                               | 32  | 49 | 66 | Slight             |
| Soft         | 10    | 50                                               | 100 | —  | —  | Heavy              |

It seemed a feasible proposition to coat paper with effective insecticidal coatings by normal industrial processes, so long as due regard was paid to preventing the insecticide being locked up within the coating. Such coatings might be applicable to decorative wall-papers as well as packaging paper.

2) *Wall paints* or coatings for furniture on which flies or mosquitoes were likely to rest, have been manufactured by licensed paint companies, following a number of satisfactory field trials in cockroach control in ships.

Trials in two ships will serve to illustrate some of the information obtained.

A clear lacquer containing 10% Dieldrin and 10% Aldrin in a 50/50 Urea/Alkyd was applied as a high-gloss top coat to the walls of the galley and stores of a ship during a refit. The walls were steel and already bore a white primer. No detectable bloom developed, with weekly cleanings. German cockroaches were wiped out after three days and failed to reinfest the treated rooms for the following 14 months. Cockroaches, houseflies and flour beetles which were brought on board during the normal activities of the ship at ports in tropical countries were all killed within a few days.



Records kept by the ship on data sheets provided showed that after 12 months houseflies were surviving in the galley for longer periods. This information coincided with check tests made in the UK laboratory showing a reduction in the vapour toxicity of the coating after that time. Cockroaches remained plentiful in parts of the ship which had not been treated. In another ship the holds and galley were coated with the harder coatings, 10% Dieldrin 2% Aldrin and 60/40 Urea/Alkyd resin and 20% DDT 2% BHC in a similar lacquer. Houseflies taken to the ship in a UK port after seven months showed that the Dieldrin/Aldrin coating was non-toxic while the DDT/BHC coating showed a bloom and high toxicity, although there was no vapour toxicity.

#### TOXIC HAZARDS OF UF INSECTICIDAL COATINGS.

Before considering applications of these insecticidal coatings, something must be said of the hazards of this means of pest control.

It seems likely that the insecticidal coatings will find their place on those semi-permanent surfaces which may serve as resting places for insect pests. For the walls, floors or ceilings, therefore, of kitchens, canteens and stores of all kinds, it will be possible to offer a range of coatings heavily loaded with insecticides to replace usual paints which will remain poisonous to insects either by contact or by emanation of vapour for periods of years rather than months, in spite of frequent washing of the surfaces. In situations where ventilation is normally thorough and continuous as in ships, the dangers are probably no greater than in the case of insecticides used in traditional ways.

Although some emphasis has been given in this investigation to the vapour toxicities of insecticides, this has been done for general scientific reasons rather than purely toxicological reasons. Volatile insecticides like Aldrin and  $\gamma$  BHC are lost fairly rapidly to the air from wettable powders, and oil solutions probably more readily than from UF coatings, but they would go on escaping from the latter for a much longer time.

Except for certain specialized packaging applications it may be doubtful whether the use of UF coatings for insect control would be economic for periods of less than nine months. In ships for instance, the galleys need redecoration roughly every nine months.

The Council on Pharmacy and Chemistry of the American Medical Association (<sup>28</sup>) has published recently a special report on the health problems arising from vaporizing devices for insecticides, from which

it is evident that continuous exposure over long periods to the vapours of  $\gamma$  BHC caused toxic symptoms in humans. The American recommendation for thermal generation of DDT insecticides is that it should not exceed 1 gm per 15,000 cubic feet per 24 hours; and for  $\gamma$  BHC from 1 gm per 1,000 cu. feet is allowed not oftener than at two week intervals. A standard formulation of UF resin containing 10% Aldrin on the resin solids would give approximately 300 mgm/sq.ft Aldrin at 1 oz. resin solids per square yard. Under practical conditions this has been found to last just over 12 months, and this would give an arithmetical mean loss of Aldrin vapour from the walls of approximately 6 mgm per sq. ft per day. This loss could be reduced to any rate down to zero with adjustments of the formulation and method of curing. Again, the area of wall treated could be reduced so long as insecticidal efficiency was not sacrificed. It is evident that different practical conditions might require different formulations in order to satisfy problems of toxic hazards, and the solutions to these problems can probably be best obtained by properly controlled field trials.

It may be pointed out that the thermal generators of insecticides referred to in the American report produce often not true vapours but aerosols or wet droplets of insecticide which after settlement on various surfaces crystallize out into solid deposits. The emanations from UF coatings are true vapours and it is virtually certain they would remain as such and would not produce solid crystalline deposits under virtually all foreseeable conditions of housefly and mosquito infestation.

#### SUGGESTED APPLICATIONS OF UF COATINGS FOR FLY AND MOSQUITO CONTROL.

##### 1) *Larvicides.*

UF coatings containing Dieldrin, DDT or BHC might perhaps be applied to underwater surfaces of metal, wood or wire-netting in the manner described for marine anti-fouling coatings (<sup>29</sup>, <sup>30</sup>) in order to maintain a level of insecticide in the water toxic to mosquito larvae. Only relatively shallow water could possibly be controlled in this manner, such as in ponds, ditches, water-butts and storm-water drains.

10% Dieldrin in UF lacquer applied to wire-netting could be expected to remain effective for several seasons.

##### 2) *Adulticides.*

Use of the coatings would fall roughly into two categories:

(a) situation where paint is in normal use

(b) situations where paint is not in normal use.

Where paint is in normal use, the usual top coat can be replaced by a clear or pigmented UF coating on walls, flooring or ceiling. The precise formulation would be made to fit the duration of intervals for redecoration or residual insecticidal action.

Where paint is not normally used, e.g. in mud huts, localized applications might be justifiable, i.e. by brush to the rafters, poles, and a continuous band one foot wide around the top and bottom of the walls.

Where renewal of the wall surface occurs at relatively short intervals because of local customs or other reasons, it is suggested that bands of coated paper, possibly in an attractive colour, could be hung around the top of the wall. This paper could then be replaced after each redecoration or refacing of the wall. This method lends itself to the best use of one of the most effective insecticides for killing mosquitoes, i.e.  $\gamma$  BHC (LINDANE), as this could be sealed in the UF coating by ultra-violet irradiation in order to provide residual toxicity over a really long period. Paper coatings of this type are easily manufactured.

A great advantage of prefabricated coatings is the freedom it confers from spraying gear, transport and mixing of powders, solutions etc. By taking a ready-made surface to the site of action, the insecticidal potency is made independent of local variations of surface type which normally affect insecticide residues.

Situations which are naturally attractive to mosquitoes or flies such as sleeping quarters, rubbish bins or meat-safes would be suitable for introducing coatings on to mosquito-netting, lining the interiors of bins, or coating the surface of metal or plastic screens.

Costs of UF coatings vary according to quantity but the following prices in UK may be quoted for guidance.

Air-drying clear lacquers, applied by brush or gun.

|                                  |                  |
|----------------------------------|------------------|
| 20% DDT . . . . .                | 50/— per gallon  |
| 2% Aldrin . . . . .              | 50/— per gallon  |
| 10% Dieldrin tech. . . . .       | 70/— per gallon  |
| 10% Aldrin . . . . .             | 50/— per gallon  |
| 5% Pyrethrines . . . . .         | 350/— per gallon |
| 40% Piperonyl butoxide . . . . . | 350/— per gallon |
| 5% Lindane . . . . .             | 75/— per gallon  |

KRAFT paper, 30 inches wide, coated with 5% LINDANE in UF lacquer, £ 20 per 1,000 yards.

Comparative costs with traditional types of insecticidal residues are

not simple because the latter vary from place to place. It would be difficult to equal the economy of insecticide used in UF coatings after a minimum period of, say, nine months. 10% Dieldrin i.e. 300 mgm/sq. if in a ship's galley washed weekly for 14 months was still killing all cockroaches and weevils. This would be roughly equivalent to 60 sprayings at weekly intervals of 5 mgm Dieldrin per sq. ft.

Finally, the preparation of insecticidal coatings on paper would be by industrial techniques, amenable to routine biological and chemical checks, giving precise accurate dosages of insecticide per unit area, in contrast to the application by unskilled labour of dosages which are known to vary enormously due to faults in spray-gear and other causes, of wettable powders or solutions.

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