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Options for Ensuring Quality in Stored Pesticide Products

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OPTIONS FOR ENSURING QUALITY IN STORED PESTICIDE PRODUCTS

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1. ***SUMMARY***

The aim of this paper is to examine various options for dealing with the problem of ensuring that a stored pesticide product is suitable for use.

The major difficulty stems from the nature of the pesticide market itself, where the handling and storage conditions are not only highly variable but are usually beyond the control of manufacturer. Under these conditions, no simple label information such as a shelf life or an expiry date can offer any guarantee of performance. However, the "lot number" is considered to be essential information for inclusion on a package since it can be used as an aid in tracing the history of a product, should questions arise. In addition, a "date of test" may also be of value, both to those in the distribution chain and to the end user, by enabling a more disciplined management of stock.

It is emphasized that good stock management, care during transport, comprehensive label advice and adherence to this advice are the best ways of assuring that products will perform in accordance with customer expectations.

Re-testing of pesticides stored for long periods is strongly recommended to assure conformance to published or agreed specifications and to minimize unnecessary disposal.

2. ***INTRODUCTION***

Modern pesticides are usually complex mixtures of different organic and inorganic compounds, including both active ingredients and inert materials. Over time, such complex mixtures may undergo chemical and/or physical changes. Moreover, one of the more desirable characteristics of modern pesticides is that they are specifically designed to have a limited persistence in the environment. This benefit may, to a degree, also limit the stability of pesticide products in storage. The rate at which these products undergo changes depends very much on the nature of the active ingredient(s), the formulation, the packaging and notably, the storage conditions. These parameters are determined for each individual product by conducting intensive storage stability studies. This important phase of development work aims at and results in the characterization of product stability under a series of well defined conditions.

In their legitimate desire to ensure that pesticides deliver optimum performance, registration authorities and other public organizations like to obtain a guarantee from the manufacturers that products will remain usable after a specified time in storage (often 2 years). Likewise, the user at the end of the distribution chain is also interested in product quality.

However, time alone is not the only controlling factor in the rate of any chemical and/or physical changes that may occur. A rather simple example demonstrates this. If cement is stored under dry conditions, time has no affect on its shelf life. However, under humid conditions, cement, stored in a paper sack has a very short shelf life indeed. The situation with pesticides is of course very much more complex, as far more parameters influence shelf life, particularly the temperature.

It must be recognized that the manufacturer loses effective control over a product once it enters the distribution chain. Once this control is lost, the manufacturer can no longer guarantee shelf life. Between the two ends of the chain, manufacturer and the user, all who are involved in distribution, handling and storage of pesticides are responsible for ensuring adherence to recommended procedures.

This paper is divided into two principal parts. The first is an analysis of the current situation regarding factors influencing shelf life and, the second looks at several proposals for ensuring that the end user is provided with a product of satisfactory quality, based on criteria that are scientifically valid, consistent and easily implemented.

3. *FACTORS INFLUENCING SHELF LIFE*

3.1. Definition of Shelf Life

The shelf life (or storage life) of a material is the period of time during which it may be stored and remain suitable for use. (Webster's Dictionary)

For a pesticide product, the "material" is the formulation kept in its original, unopened and undamaged package. "Suitability for use" means that at any time during a defined period, the formulation fulfils the following requirements:

i. It has not undergone any changes that would result in an increased hazard to the user.
ii. It has not undergone any unacceptable drop in biological efficacy due to either an excessive decline in active ingredient content or physical changes in the formulation.
iii. Its physical properties are such that it can be completely and easily applied with standard or stipulated application equipment.

3.2. Storage Stability Studies

Pesticide manufacturers recognize that it is in their own interest to have reliable information on the storage properties of their products. As the distribution of many pesticides is world-wide, the variety of different climatic conditions under which products are likely to be stored must be taken into account during the development of new pesticide formulations. Industry, therefore, carries out storage stability tests under well defined and controlled conditions at both ambient and elevated temperatures. Low temperature studies are normally included for liquid products, particularly if they are to be shipped through, or stored in, areas with cold climates. The goal of these tests is to evaluate the storage properties of a product as well as to identify suitable packaging materials. From the data obtained under these controlled conditions, a prediction of minimum storage stability under proper storage and handling conditions can be made.

If chemical stability is the limiting factor in a product's shelf life, it must be kept in mind that the rate of degradation is a function of temperature. From kinetic studies it is known that the rate of decomposition practical implication is that a product with a shelf life of 5 years at an average temperature of 20°C may have it reduced to 2 years or less at an average temperature of 30°C.

Normally the following tests are conducted:

i. Samples are stored at room temperature and at 30 - 35°C (to simulate tropical conditions) for a period for which the product is to be guaranteed (e.g. 2 years).

ii. In the case of new products for which such long term data are not yet available, results of tests on samples stored for 3 to 6 months at room temperature and at 30 - 40°C in accelerated tests are usually considered satisfactory at the time of registration.
iii. The CIPAC Heat Stability Test (Ref. G.) which specifies storage for 14 days at 54°C may also provide useful information.

The environmental conditions of the test and the containers used should be described in the results of all tests.

Where possible, commercial packaging is used in the studies. All samples taken are examined for appearance, physical properties, a.i. content and, where relevant, for decomposition products (See Ref. G). The containers are also inspected for corrosion and other effects.

3.3 Transport and Storage Conditions

World-wide distribution of pesticide products results in their exposure to a wide variety of conditions of temperature and humidity.

These may vary considerably, not only from country to country but, also from season to season. A manufacturer tries to encompass all these variations in estimating a minimum shelf-life but any conclusions drawn regarding stability become invalid if unpredictable and additionally unfavourable conditions occur.

Such unfavourable conditions include but are not limited to:

i. Storage and transport in direct sun.
ii. Excessive heat in a sealed shipping container or in a poorly ventilated warehouse.
iii. Corrosion of the exterior of containers due to poor warehouse maintenance or as a result or exposure to seawater and rain while deck loaded on ships (required with some pesticides) or other vessels.
iv. Damage to protective internal coatings on containers as a result of rough and improper handling during transport.
v. Corrosion of containers due to spillage from other containers nearby.

Many unpredictable factors influence whether and for how long products are subjected to such unfavourable conditions during transport and storage.

3.4 Factors Limiting Shelf Life

It is self-evident that the shelf life of a product will be determined by the least stable physical or chemical parameter, that is, the parameter whose value is the first to fall below the minimum acceptable limit. Therefore, in

estimating shelf life, a decision must be made on the acceptable limits (tolerances) on the product-specific properties measured.

For example, it is generally accepted that a decrease of 10% of the declared a.i. content will not significantly influence biological activity and this limit is usually considered acceptable by FAO (Ref. G).[1]

The physical properties of a formulation influence primarily its application performance (e.g. emulsion stability, dispersibility, etc.).

However, experience has demonstrated that that application performance of a product cannot, in most cases, be nearly as well correlated to the physical properties as efficacy can be to the a.i. content. The physical property specifications needed may be largely dependent on application techniques and equipment available. Furthermore, there appears to be no good correlation between the laboratory determined physical stability data and the actual application performance in the field. Thus, it is almost impossible to extrapolate from the experiments performed in the laboratory to the application behavior of a product stored under a variety of unknown conditions in the marketplace.

3.5. Conclusions on Shelf Life

After evaluating the results of stability tests, the shelf life of a pesticide can, based on a relatively small set of laboratory data, be predicted with a fair degree of precision for defined conditions. However, as described, actual conditions of transport and storage can vary considerably. Therefore, since the figures derived from laboratory tests, and those derived from tests under local ambient conditions cannot cover all possible variations, only an approximate shelf life can be predicted. It is impossible to predict the precise shelf life of individual product batches because of the diversity of conditions to which they are exposed in the marketplace.

4. EXISTING APPROACHES TO ASSURING QUALITY AFTER STORAGE

Many individual countries and/or international organizations have tried to solve the problem of providing effective products to the end user by making some specific recommendations or by introducing regulations (Ref. A, B, E, G). These current measures and their consequences are outlined in the following sections.

[1] Chemical changes may influence the toxicity of a product. However, toxic decomposition products are rare, and are characteristics of particular active ingredients (a.i.). Limit must, therefore, be set on a case by case basis.

4.1. Expiry Date

In theory, the expiry date is the last date that a product, when used according to the directions on the label, can be applied normally and also retain the expected biological performance without undue deleterious effects (e.g. phytotoxicity, etc).

It would seem that a clear expiry date on the label is advantageous for both the dealer and user in that both would know that they had received a fresh product (provided the pesticide still is in its original unopened container or has been properly repacked and relabelled). However, it has been pointed out that shelf life and hence, expiry date depend very much on actual storage conditions, especially on the level of, and the fluctuation in, temperature and humidity (depending on the formulation).

Consequently, it is not possible to establish one single date for expiry for products that may go to a variety of different regions and there be stored under highly variable sets of conditions.

From a scientific standpoint it would be logical to assume a set of "desirable" and "worst case" conditions and thereby estimate the range of extreme values for expiration date but, double dating does not provide useful information.

If, on the other hand, the date of expiry is based solely on the "worst case" scenario of storage conditions, the user would be guaranteed a good product but, since the worst case is seldom encountered, products still in good order would have to be disposed of. Disposal of legally expired but technically satisfactory pesticides would have two over-riding disadvantages:

i. Pesticides are expensive agricultural inputs to the farmer and disposal of perfectly good pesticides removes the possibility of anyone benefiting from the product and would result in a general increase in cost to the end-user.
ii. Pesticides are, by definition, biologically active compounds and if stored or disposed of improperly may represent a significant and unnecessary hazard to man and the environment.

Thus the printing of a clear expiration date on the label, although it may seem to be a simple and safe means of assuring the user that a pesticide is still good, would create more serious problems than it solves.

4.2. Manufacturing Date

The advantage of using a manufacturing date is that it would help in stock control using the "first in-first out" system.

Another advantage is that, compared to the use of an expiry date, it does not automatically designated products, which could be usable, as unsaleable and therefore ready for disposal. However, it is obvious that a manufacturing date cannot in itself guarantee that a given pesticide is still suitable for use months or years after its manufacture.

A significant disadvantage of using the manufacturing date alone is that it does not, in itself, identify individual batches. But, the major disadvantage of a manufacturing date is found in human nature. The user, in assuming that the latest dated product is somehow fresher and thus better, may leave behind somewhat older but perfectly good product, ultimately creating serious disposal problems at the end of the distribution chain.

4.3. Date of Test

In recent WHO specifications a "Date of Test" is required on the label (Ref. E). It is to indicate the date on which the product was found to be in compliance with the given specification.

Such a "Date of Test" is scientifically valid, elegant and reasonably easy to utilize at all levels of distribution, provided adequate test methods are available. It is preferable to the use of manufacturing date since it indicates that on the date in question the product was found to be in compliance with a specification. This could be at the time of manufacture or at any time thereafter.

5. PROPOSALS FOR ASSURING QUALITY AFTER STORAGE

It is evident from the preceding sections that the problem of assuring quality to the end user is complex and, unfortunately, requires a complex solution. The solution has to be based on a whole set of measures that must be fully implemented in order to obtain optimum results.

5.1. Manufacturing Lot Identification

The "Manufacturing Lot Identification" identifies individual batches and is required by law in many countries. It should always be printed either on the label or on the container (Ref. A). The number can be used to trace the history of a product, should this be required.

5.2. Good Housekeeping and Transport

Good housekeeping rules for storage and transport (Ref. F) should include the following elements:

i. The use of properly constructed and maintained storage facilities that will provide the coolest and driest storage conditions possible.

ii. Strict observance of all storage instructions on the label (i.e. read the label).
iii. Strict use of the "first in-first out" system of stock management.
iv. Encourage the use of the entire contents of a package once it is opened. (To achieve this goal, suitable package sizes should be provided. Where this is not possible, packages should be recloseable and reclosed tightly after use.)
v. Avoid failure by eliminating:

- transport and storage at extreme temperature
- corrosion of containers from without
- undue mechanical handling of packages (See 3.3)

5.3. Specifications

The available FAO Specifications should be more generally accepted and utilized. If these are not available, product-specific and realistic specifications based on agreed FAO Model Specifications and available test methods (CIPAC, WHO, AOAC) should be developed and used (Ref. B, E). Packaging specifications should be based on the actual transport, storage and climatic conditions that may be encountered.

5.4. Guidelines for Special Conditions

In exceptional cases, and only where the stability of a product is considerably less than that which might reasonably be expected by a customer (normally 2 years under cool, dry conditions and in an original unopened package), guidelines on the label should contain an expiry date.

Such guidelines may also include recommendations concerning maximum storage temperature and time (e.g. "Avoid temperatures above 40°C; use within one year").

5.5. Re-Analysis of Stocks

Keeping in mind that the best "disposal" method is the normal use of the product, it is strongly recommended that instead of being removed from the market disposal, stocks be re-analyzed (with proper sampling procedures) to determine if the material is still fit for use. In most cases the cost to the customer for an analysis would be negligible compared to the value of the merchandise plus the additional cost of proper and possibly unnecessary disposal.

Disposal of a pesticide should always be considered a last resort.

Stock should be re-analyzed after:

i. extraordinary long storage

ii. storage under unfavourable conditions
iii. when the expiration dates that may be required by national legislation have been exceeded.

Any analytical results must be interpreted for the user by a competent local service laboratory. Products can then be classified into three categories.

I. Specifications are met fully; the stock can be re-labelled with the date of the test and the product can continue to be stored.
II. Some deterioration (such as is sometimes noted after heat tests) has occurred; product can still be used within a short period of time.
III. Deterioration of the physical properties and/or of the a.i. content have significantly exceeded the limits in the specification; the product can no longer be used and must be disposed of.

(Guidelines for such classifications may be obtained from either published product specific specifications (e.g. FAO, WHO, national government specifications) or from manufacturer's specifications when no such published specifications exist).

6. ***RECOMMENDATIONS***

Based on the preceeding, it can be concluded that the complex problem of ensuring that an end user is provided with a good pesticide product requires a complex solution. Assuring quality after storage depends on following a complete set of principles for handling, storage and quality control.

The establishment of a formal expiry date for each product is a simplistic approach and inevitably will cause more problems than it resolves, both from the financial loss standpoint and by creating unnecessary disposal requirements.

As a consequence, it is recommended that:

i. All products be identified by a lot number.
ii. Labels should contain information on appropriate storage conditions.
iii. Products be handled and stored in strict accordance with good housekeeping and transport practices.
iv. Stocks should be re-analyzed where the quality of a product is suspect due to prolonged storage and/or unfavourable storage conditions and the date of the test should appear on the product label.
v. Realistic specifications on which to base an evaluation of product quality after re-analysis should be available.

7. ***REFERENCES***

Different international organizations have dealt with the problem of labelling, storage, and handling of pesticides. A number of publications contain information on these topics.

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