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THE CONTROL OF BIODETERIORATION BY FUNGICIDES—PHILOSOPHY

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Summary

Factors governing the correct use of fungicides have been described previously and are reviewed briefly. The development of fungicides for commercial practice is dependent on a philosophy that varies with the groups involved in the exploitation and use of the compounds. Objectives and requirements for fungicides as seen by the producer and user often are not the same. Reconciliation of differing views therefore depends on a dispassionate assessment of the final use requirement. Compounds that exhibit an inherent lack of ability in meeting requirements may sometimes be improved through proper formulation. Often, however, formulation efforts to overcome inherent weakness in a compound yield marginal improvements, since the weakness lies within the chemical structure of the compound. The basic chemical structure is then altered to try to improve specific properties. This approach also meets with different degrees of success. Any attempt to improve functionality requires determination of exact capability of a given compound and an understanding of the limits imposed on its use. With facts in hand improper attempts to force compounds to perform efficiently in situations contraindicated by the nature of the compounds can be minimized. Examples illustrating these points will be given.

INTRODUCTION

During this Symposium there have been sessions concerned with fundamentals and mechanisms of biodeterioration, and this one is devoted to the control of biodeterioration. As the introductory speaker, I propose to discuss in general terms the philosophy of biodeterioration control, relative to control by fungicides, since this aspect will readily illustrate the points I wish to make—and will probably be of greatest interest to most in attendance. The thoughts, however, are germane to other control techniques, where a number of different industries or technical organizations are involved together in rendering materials resistant to microbial attack. Protective techniques and compounds will only be mentioned as they support the various theses presented. I anticipate that other examples will become apparent during the Symposium in papers that concern themselves with specific means of deterioration prevention.

Choice of a fungicide to prevent microbial degradation of materials is seldom simple. Not only must the specific material and its contemplated use be known but physical and chemical conditions encountered during manufacture of the material or item, compatibility of the fungicide with other treatments being applied, color, odor, toxicity and economic requirements, must all be considered in the selection and decision-making process. The interplay of these factors in meeting requirements and selecting the correct treatment has been discussed in a previous publication, Kaplan (1967), and will not be repeated. Requirements for fungicide treatments change from case to case and these may be as numerous and varied as there are materials, formulations and use conditions. Despite this, it would appear that parameters governing the selection of proper fungicides could be clearly defined for each circumstance thereby indicating types of fungicides that should be considered, if not specific compounds. Theoretically, one should be able to establish a computer program listing all the known requirements, include a data bank of fungicides of varying characteristics, press a few buttons and the proper answer should be forthcoming. However, the answer depends on the data available to the computer and thus on the correct and full identification of requirements and fungicides. It is here that difficulty arises. Who makes the necessary identification and judgement? Individuals having an interest in ensuring serviceability of materials may fall into as many as 6 categories—those who design or engineer a material for a given use; the producers of the fungicide; the formulators; the fungicide users who produce a treated material or component; and those who use the fabricated item. For each of these groups the ultimate objective appears to be the same, namely adequate protection of the fabricated item. But it is in the definition of the term 'adequate protection' that differences in point of view come to light. At each stage in the sequence from producer to user the concept changes as to what constitutes a suitable fungicide. Judgement as to suitability naturally is influenced by and is a function of the immediate interest and concern generated by demands of the particular activity in the sequence with which the worker is involved. The way these demands affect the judgement process therefore, must be examined for each step starting with production of the material and the fungicide and ending with a treated item in use.

The focus for all considerations in prevention of microbial deterioration is the material to be protected. All materials are fabricated with functional purposes in mind. To materials and design engineers maintenance of functional properties is paramount and any secondary treatment, at best, is regarded with suspicion and, more often, resisted. This position is based on the fear that treatments will interfere with functionality, and for this there is some justification. Examples that come to mind are the adverse effects of copper compounds on certain types of rubber, change in properties of hydrocarbon fuels and clogging of combustion engines with the use of metal, halogen or sulfur-containing biocides for fuels, darkening of vinyl plastics when heat sensitive compounds are added to the vinyl mix, loss in tensile or tear strength in cellulosic textiles with the application of aminoplast resins, and corrosion of metal components when they are wrapped in paper-based moisture vapor barriers treated with copper pentachlorophenate.

At the outset, therefore, the dogma governing the actions of all involved is maintenance of *functional integrity* of the material. Any real, fancied or anticipated impairment of functionality immediately brings about rejection of the concept of protection of the material, hence engineers attempt to introduce the material with either no treatment whatsoever, or, with only partial protection. If the material is susceptible, however, the ultimate user of the material will establish the need for treatment, but the designer limits the nature of the fungicide that can be considered.

THE PRIME PRODUCER

The fungicide used is generally the product of a company that has its prime capability in certain types of chemicals, *i.e.* phenols, organometallics, halogens, etc. The fungicide may be part of the main stream of the company's production or it may be a by-product. The compounds produced by the company may be sold for a number of purposes. For example, organotin compounds are used as stabilizers for plastic formulations, as rodent repellants and as fungicides; mercaptobenzothiazole and other organic sulfur compounds are rubber stabilizers as well as fungicides. As a biocide the compound may find application in pharmaceutical and agricultural areas in addition to industrial material uses. Under the foregoing circumstances the fungicide that is offered as an article of commerce may have its physical and chemical properties determined by the requirements of its greatest commercial demand, and this may not necessarily be its use as an industrial biocide: or its characteristics may be fixed by a manufacturing process that cannot be changed to accommodate the secondary demand of a by-product. The basic material as presented to the formulator may not be necessarily in the best physical or chemical state for any intended use. Even if a product demonstrates proper antimicrobial properties in laboratory tests, it may be lacking in certain other non-biological attributes.

A case in point is copper naphthenate. Commercial copper naphthenate is made by reacting copper salts with undefined mixtures of naphthenic acids obtained as by-products during petroleum refining. Biologically speaking, various commercial mixtures generally appear to be equally effective, but all preparations of copper naphthenate have not been found suitable for textile treatments. Commercial preparations have varied considerably in odor ranging from acceptable levels to highly objectionable. Early literature, as reported by Greathouse and Wessel (1954), gives conflicting reports concerning the adverse effect of copper naphthenate on cellulosic materials when treated materials were exposed to weathering. Siu (1951) commenting on actinic degradation by copper naphthenate states, 'It must be remembered, however, that the above results have been obtained with commercial samples of varying quality of copper naphthenate. One cannot draw rigorous conclusions regarding the photochemical catalysis by such data. It is highly probable that the positive results with commercial products reflect the presence of the unreacted inorganic copper salts which are known to be catalytic in this respect. Accordingly, the purer the naphthenate sample the more inert should its behavior be towards the photochemical degradation of cotton fabrics.' With this preservative past deficiencies evidently have been corrected since present day commercial preparations, evaluated in our own laboratories as recently as 1966–67, showed no degradation of cotton duck after 8 months outdoor weathering at Maynard, Massachusetts, and odor of the treated textile was not excessive. Presumably greater care in choice of distillation cuts of naphthenic acid and preparation of the copper soap have accounted for the generally even performance now observed.

One may also consider creosote here. Creosote is a distillate from coal tar, a residual product of the carbonization of coal obtained during high temperature (1000°C) production of metallurgical coke at intermediate temperature during the production of municipal gas from coal. Baechler (1967) notes that the chemical nature of coal tar varies with several production factors of which temperature and time are most important. At carbonization temperatures of 500°C–600°C the tar contains relatively high amounts of aliphatic hydrocarbons and acidic oxygen containing compounds that are designated as tar acids. As carbonization temperature is increased the percentage of aromatic hydrocarbons is also increased at the expense of aliphatic or saturated cyclic hydrocarbons and tar acids. Coal tar distillate from 200°C to 400°C is sold as creosote. Lower boiling fractions may be processed for recovery of naphthalenes and tar acids and the processed cuts then blended with the higher boiling cuts.

Under these conditions, the product offered as a preservative is that which results from manufacturing practice. There is no standard preparation universally available although efforts are made to identify and specify various cuts through distillation analysis. Such considerations are academic, however, since there is little agreement regarding the exact characteristics for an effective preservative. The relative merits of high and low temperature produced creosotes are still being discussed.

The examples given should not be used to infer that each and every fungicide is a product which is offered on an 'as is' basis, take it or leave it. They are first examples, showing that the word 'suitable' does not mean the same to all involved. In this instance, the prime producers undoubtedly feel that their products can perform well but the true question to be answered is—how well? The manufacturer of the basic chemical is satisfied that the product is fundamentally sound and will perform quite well if properly used. He is not alone in this opinion. His views may be shared by those next involved, namely, the organization that formulates the fungicide, however imperfect, to permit it to meet application and field requirements.

THE FORMULATOR

In the United States, the company making the basic chemical may not necessarily formulate the fungicide for specific uses. Frequently the formulation of a fungicide passes on to a company whose sole function is the development of formulations for specific applications required by its customers. The objective in preparing formulations again is to provide a suitable fungicide. In reaching this objective a philosophy is encountered that is inherent in a formulator's situation, namely that through the alchemy, art and science of formulation, a given fungicide can be made suitable for many, if not all, situations. Further, if a fungicide has a weakness integral with its chemical nature, this can be overcome practically to provide a workable fungicide. Thus some fungicides are insoluble in water but soluble in non-polar solvents. The answer is to formulate a water-miscible emulsion. Some fungicides tend to aggregate into crystals, and migrate or bloom to the surface. The solution is to include an anti-blooming agent in the formulation. Some fungicides are light-sensitive, which is overcome by adding an ultraviolet absorber to the formulation. Some fungicides hydrolyse with the production of acids which will damage the treated material, hence acid neutralizers are required. Finally, some fungicides are soluble in water, and water repellents are supplied to prevent loss under wet situations. With all of these aids it would appear that a given fungicide could be used universally, but not so.

For example 2, 2′ methylene-bis (4-chlorophenol) is readily leached from textile materials. Efforts to prevent loss through the incorporation of water repellent compounds or binders in formulations are not wholly successful. In our own laboratories we have encountered losses of this fungicide varying from 50% to 85% in fabrics treated with a variety of water-repellent compounds when leached according to our standard textile leaching procedure (Textile Test Methods 1951). A larger amount of this fungicide therefore is specified for treatment of many of our materials to make certain that an effective residue remains when the material is exposed to water.

Pentachlorophenol and its derivatives, rosin amine D pentachlorophenate and lauryl pentachlorophenate, break down under sunlight, leading to the formation of compounds which damage cotton textiles. Over the years we find that this undesirable feature cannot be succesfully overcome through the use of ultraviolet absorbers, either in a formulation of these fungicides or when added separately to the treated materials.

As formulations become complex, behaviour of the entire formulation may be affected due to ingredient incompatibility. Sometimes the formulation requires so sensitive a balance between ingredients that deviation in ingredients brings about functional weakening of the product's properties. Formulation ingredients may be changed due to economic factors and alternate ingredients substituted if the price of the desired ingredient becomes too expensive. Patent considerations also affect the performance of a formulation since ingredients or processes may vary based solely on patent coverage with resulting differences in formulation performance. Bomar (1966) cites a number of references where surface-active agents diminish the antifungal activity of some preservatives. He presents experimental data showing that surfactants used to provide a homogeneous dispersion of water-insoluble fungicides may interfere with inhibitory activity of copper pentachlorophenol and copper 8-quinolinolate. Adema, Meijer and Hueck (1967) studying low activities of certain lauryl pentachlorophenate preparations found that the purified lauryl pentochlorophenate did not show as effective biological activity as technical grade formulations containing some residual pentachlorophenol. Kempton, Greenberger and Kaplan (1962) carried out extensive chemical analyses on 10 samples of webbing which had been treated with a number of formulations of copper 8-quinolinolate. It was determined that the preparations contained copper other than copper 8-quinolinolate and in one instance 56% of the copper in the webbing was in the form of a compound other than the 8-quinolinolate chelate.

If it is recognized that a weakness may not be corrected by formulation, the next approach is to alter the fungicide molecule to provide related compounds that correct the deficiencies of the parent compound. Patent and scientific literature are full of examples of such derivative compounds, including a wide variety of substituted phenols and organometallic compounds. Metals, halogens, nitro or sulfur groups are incorporated into basic fungicide moieties in infinite combination, molecular weights and chain lengths are increased or decreased, molecular configurations are altered and molecules are chemically linked in one fashion or another. These variants are then incorporated into formulations and the newly acquired virtues offered as improved products. In some cases this approach does provide beneficial attributes, often the improvements are marginal. Dahl and Kaplan (1961) studying a number of organic amino acid compounds found that 5,6-dichloro-2-benzoxazolinone indeed was an effective leather fungicide where 2-benzoxazolinone,2-amino-4,5-dichlorophenol,2-aminophenol,4-aminophenol,2-aminopyridine,2-aminobenzoic acid and 2-aminobenzimidazole were either completely ineffective or poorly effective. On the other hand substitution of copper by other metals to provide colorless naphthenates or chelates of 8-hydroxyquinolinolate results in compounds with decreased antimicrobial activity in most cases. Similarly, alterations in the organic moiety of organomercurials or organotins generally do not increase resistance of these fungicides to weathering stress, Dunn and Hill (1967).

From the preceding discussion it becomes obvious that the formulator's judgement as to suitability must also be accepted with provision for natural bias based on the function performed by this group. This is not to say that the formulator's position is fundamentally suspect. Certainly, without the formulator's endeavors our present efforts to prevent deterioration would be hampered. The formulator's contribution, however, is not a universal panacea justifying exclusive reliance on his judgement concerning functional adequacy of a formulated fungicide.

THE TREATER'S ROLE

The roles of the prime producer of the fungicide and the formulator in the process of providing microbially resistant materials have already been emphasized. The fruit of their labor finds its way to a third party—the treater who will apply the formulation to a material. The prime consideration of the treater is economy—economy in material cost and economy in application, and a delicate balance exists at this point between economy and quality. In some circumstances fungicide content of the treated material is specified, in others evenness or thoroughness of treatment is required, and, in still others, no level is specified beyond the vague requirement that the material must be protected by a suitable treatment. In the treater's eyes a material is adequately protected if it meets the stated requirements as set forth in the procurement contract. It is to his advantage to perform the treating operation as tightly and economically as he can, yet still stay within his contractual obligation. To do this he tries to stay close to the minimum deposition required, if any; he looks toward the simplest means of applying the compound with his existing equipment; seeks to combine the fungicide with other finishes to achieve treatment with one pass through the machines; and keeps preparation of materials to a minimum and operates his machines at the greatest speed possible. The treater judges a treatment to be satisfactory in terms of his ability to apply the treatment profitably within the capacity of his production facilities. Indeed, his entire approach is defined or limited by the equipment available. Application of a given formulation, therefore, will vary depending on the treater, with variations obviously occurring as a reflection of the conditions employed. In one instance the treatment may indeed meet all requirements, in another it may not. A thread may be tightly wound on a cone being dipped in a treating solution rather than as a loose skein; the pressure chamber of a wood treating plant packed very tightly with no provision for adequate spacing to insure even circulation of the preservative; a pretreatment required to insure an even application of fungicide to a fabric too quickly and therefore poorly done, or a superficial surface treatment applied where penentration in depth is required. Knowing the treater's policy, there can be no complaints if the buyer has not had the foresight to stipulate quality control safeguards.

THE MANUFACTURER

In most instances, treated material is utilized as a component of an item or a system. A textile may be used as a component of a tent, a coated fabric as part of a mine conveyor belt or life raft, a treated plywood panel as a component of a refrigerator or a packing crate, a treated timber as a part of a structure, a plastic as a part of an electric cable or an electronic module. The material therefore passes on to the next interested party—a manufacturer who assembles a number of materials into a finished product. The various materials go through handling and processing procedures involving both hand and machine labor, and rate of production of the product is an important part of a profitable operation. Should a treated material interfere with a production schedule, then that material is simply not suitable as judged by the interests of the manufacturer. Fungicidally treated materials may, indeed, interfere with production schedules. For example, chlorinated phenolic compounds are irritating to humans and have in the past interfered with assembly line production of some items that involved human handling operations by causing skin or eye irritation. This problem can be corrected by use of standard industrial hygiene practices such as provision for adequate ventilation and the use of protective clothing, *i.e.* gloves and aprons, as well as closer quality control by the treater to be certain that levels of fungicides in the material do not exceed required tolerance. Nevertheless, the manufacturer is disturbed if he must take special precautions or install special equipment, and his understandable reaction is to look for another fungicide that will not add to his problems. In such cases a material treated with an alternative compound that is 'just as good' may be supplied to the manufacturer. But is it just as good? For the treater of the material—yes, for the manufacturer of the item—undoubtedly. For the ultimate user? Perhaps.

USER-REQUIREMENTS

Finally, we come to the individual who makes binding judgement as to adequacy and who is the actual user of the item or system concerned. Whatever the circumstance or product, the fungicidal treatment is successful only if it meets the users requirements. These requirements may be minimal or may be extremely rigid and severe. In one instance, accommodation of the thinking of the various groups discussed can be tolerated by the user and the situation is happy since no particular problem arises to plague anyone, from prime producer of the fungicide through to the user of the item. On the other hand, the user may find that the item does not meet his requirements because he cannot tolerate the final result of what others judge to be satisfactory. In this situation it must be axiomatic that the users criteria are those to which the others must accommodate, if at all possible.

However, this may not be readily acceptable to those involved in the production chain. They may tend to confuse the only valid requirement by substituting their own judgement as seen from their own position. We have seen often attempts to force the use of a compound or treating practice where commonsense alone indicates that the effort is found to end in, at best, partial success, or, at worse, complete uselessness. For example, a number of years ago a determined effort was made to have orthophenylphenol accepted as a leather fungicide for footwear used in the field. The reasons given were many and varied, ranging from low toxicity of the compound to criticism of a standard fungicide. The basic physical property pertinent to the situation that no amount of fluent argumentation could obscure, however, was the volatility of the compound (Dahl and Kaplan, 1958). Orthophenylphenol impregnated into leather is fugitive even when boots are stored in temperate climates. Fungicides for footwear must be retained in leather for a reasonable period. Effort on the part of the supplier to have the fungicide adopted was wasted and effort on the consumer's part to prove the obvious could have been utilized more profitably.

Despite the fact that the user's requirements must prevail, the user, however, is often as much involved in problems with treated materials or systems as are the producers. Unless the user clearly specifies his needs and carefully documents his requirements he cannot fault his suppliers who have exercised their best judgement and good faith. If his only requirement is a vague statement that a 'suitable fungicide must be employed' then he has waived his judgement in favor of his suppliers, and must expect to abide by the solution, as provided from their respective positions. On the other hand, when the user exercises his responsibility by defining his requirements he must be realistic, and sometimes these may be overstated, understated, or simply misinterpreted. To require the same level of protection for an expendable wooden pallet or packing crate, as for a telephone pole or railroad tie, is as bad as requiring a superficial dip treatment instead of a pressure treatment of structural timbers in order to save on initial costs. To insist that base materials treated with copper fungicides should not be used in contact with all types of rubber is to display obstinacy by ignoring studies indicating that some butyl or neoprene rubber compounds may be used safely in contact with fabrics treated with copper 8-quinolinolate 1%.

RESOLUTION OF THE PROBLEM

The resolution of the problem lies simply in knowing and appreciating the exact capability of a given treatment and thus obtaining realistic understanding of the limits imposed on the use of the compound. Understanding is called for on the part of all those concerned with material design and the production, application and utilization of the treatment. With this understanding it may well be that the user will have to compromise his position but only to the extent that his requirements, for the moment, cannot be met. Certainly, with facts in hand, any attempts to force compounds to perform efficiently in situations contraindicated by the nature of the compounds can be minimized.

Rejection of the philosophy of truly knowing the fungicide and using it correctly will surely result in failure for, as Pasteur has said, 'Messieurs: C'est les microbes qui auront le dernier mot.'

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