HOW ADVANCES IN ALGAE-RESISTANT ROOFING ADDRESS THE GROWING ROOF ALGAE PROBLEM

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Black streaks, which destroy the appearance of asphalt shingle roof systems, are a growing problem in almost all parts of the United States. This discoloration, often mistaken for dirt or worn-out shingles, is actually the result of algae growing on the roofing granules. The most common form of algae present on roofs is known as Gloeocapsa Magna. Although this problem is most serious in the Seaboard and Gulf states, as well as the Pacific Northwest, it continues to invade other regions of the country. The presence of algae on a roof can have a number of detrimental effects, such as increased maintenance costs and reduced property value. Public awareness is increasing as products become available to fight this problem. After studying the problem for years, the authors' company has developed a thorough understanding of the problem and how to address it. This paper discusses the scope of the roof algae problem, some current attempts to prevent growth, and how the relatively new copper-containing granule works to provide an algae-resistant roof. When properly blended with standard colored roofing granules, this copper granule works on the principle of providing a uniformly distributed, controlled release of cupric ions. Research has led to a mathematical model of this controlled leach that correlates very well to real-time exposure studies of the copper granule's performance.

KEYWORDS

Algae-resistant roofing, asphalt shingles, blue-green algae, ceramic coating, copper, Gloeocapsa, roof discoloration, roofing granules, time-release modeling.

INTRODUCTION

A common problem with many types of roofing materials is the unsightly discoloration that often occurs in as little as one to two years after installation. On asphalt shingles, this discoloration can be easily identified as black or dark streaks running down the roof. The cause of these streaks or stains is often thought to be soot or dirt and is taken as an indication that the shingles may be worn out. Another common misconception is that the black streaks are due to a fungus growth on the roof. In order to begin to truly understand the cause of this discoloration, the authors' company conducted a nationwide survey and study of roofs in 1967 and a follow-up survey in the 1980s. The findings conclusively determined that, in fact, the most common cause of roof discoloration is a specific type of algae, which is not a fungus, on the shingles.[1] This alga, known as Gloeocapsa Magna, belongs to the division Cyanobacteria (commonly referred to as blue-green) in the Eubacteria kingdom.[2] Although not nearly as common as the Gloeocapsa, a second type of blue-green alga, Scytonema, was also found to be growing in the roof environment. The Gloeocapsa is a unicellular organism, while the Scytonema is filamentous (consists of finger-like strands of growth).

Additionally, it was discovered that this problem is not restricted to coastal or southern regions. Indeed, the problem is typically most severe and receives the most attention in these areas. However, significant discoloration caused by algae can be found throughout most of the United States. Algae spreads from an infested roof to other roofs via the release of airborne spores. As more and more homes have been built in close proximity to one another, algae has spread rapidly throughout entire neighborhoods. With this increasing number of infested roofs, there is an increasing amount of spores being released into the air that can contribute to the infestation of additional roofs. Furthermore, public awareness of this problem has also increased, likely because of the larger number of homes that have roof discoloration and because of the advertising surrounding products designed to prevent it. This combination of factors has resulted in an overall growth of the roof algae problem.

In response, research was conducted in order to gain an understanding of why algae has been able to thrive in a harsh environment that is often subjected to a variety of extreme conditions. Summer conditions in the United States can range from extremely hot with long dry spells and intense ultraviolet (UV) radiation exposure to heavy downpours. Winter conditions can include intense cold and thick snow or ice cover. In both summer and winter, roofs are often subjected to high winds and contain little in the way of nutrients. It was discovered, however, that this strain of algae is well-adapted to these conditions by way of a number of important characteristics that allow it to flourish in the typically harsh roof environment. Gloeocapsa and Scytonema are both desiccation-resistant organisms, which means that they can go for extended periods of time without water. They are largely unaffected by the heat and simply become dormant in the winter cold. Gloeocapsa found on the roof are shielded from intense UV exposure by the formation of a protective, heavily pigmented outer sheath material that surrounds the individual cells. In fact, the visually distracting black color of these algae is due to this sheath that encapsulates the organism. The black sheath appears to be a response mechanism to growth in the presence of intense sunlight, because if grown under low light conditions, the algae appear blue-green in color. The occurrence of a heavy downpour or high winds has little chance of removing established colonies of

Gloeocapsa from a shingle because the algae secrete a material that adheres them firmly to the shingle. Moreover, wind is important to the propagation of algae because it carries spores from roof to roof. Finally, the lack of many essential nutrients in the roof environment is overcome by the organisms' ability to obtain carbohydrates through photosynthesis and nitrates by fixing atmospheric nitrogen. Other trace nutrients not present in the shingle can be obtained from dust and dirt that settles out of the air.

Although well-suited to the roof environment, algae was found to be vulnerable to anything more than a trace amount of a variety of metal ions, such as zinc and copper. This was first suspected from the observation of algae-free regions of roofing directly below metal vents, which are often galvanized steel. In fact, the use of zinc pellets was an early attempt by the roofing industry to prevent the growth of roof algae. Although zinc can be an effective algae inhibitor if used in sufficient quantities, it tends to introduce several other problems not present with copper-coated granules. For example, zinc pellets used on shingles result in the formation of "blooms," or white spots, spreading out from the pellet because of the buildup of zinc oxide. In addition, zinc pellets don't offer the ability to produce different colored algae-resistant granules to fit with a wide variety of shingle blend designs.[3]

DEVELOPMENT OF THE COPPER GRANULE

Further study of this phenomenon involved an investigation of the mechanism for toxicity in algae, the relative toxicities of various divalent metals, and the minimum toxic concentration of copper necessary to inhibit algae growth. The results of several researchers on the toxic mechanism and the relative toxicities are reviewed in *Trace Elements in Biochemistry* by H. J. M. Bowen.[4] Bowen states that the poisoning of enzymes is believed to be the critical mechanism of toxic action. Based on this theory, much effort has been spent, with some success, to correlate the toxicities of various metals with such characteristics as electronegativities,[5,6] sulphide solubility,[7] or chelated derivative stability.[8,9,10] Based on the order of electronegativities, which is the strength with which an atom in a covalent bond can hold onto electrons, the order of toxicity for divalent metals is as follows (in order of decreasing toxicity):[4]

$$Hg > Cu > Sn > Pb > Ni > Co > Cd > Fe > Zn > Mn > Mg > Ca > Sr > Ba$$

Similar orders have been developed based on the other two factors (i.e., insolubility of the metal sulphides and chelated derivative stability).[4] The important consideration in understanding the toxic mechanism is that the metal generally is toxic to algae only if it is present as an aqueous metal ion. In the case of copper, the most important ionic form is the cupric ion (Cu^{2+}). In terms of relevance to the development of an algae-resistant roofing granule, there are two key conclusions that were drawn from this information. First, after eliminating those metals clearly hazardous to the environment, such as mercury and lead, the best remaining choice in terms of effectiveness is copper. In fact, in comparison to zinc, copper was found to be 10 times more toxic to a similar sheath-forming blue-green alga, Chroococus Paris, growing in a BG-11 medium.[11] One difficulty in drawing conclusions from this type of literature data is that although the specific algae studied is similar, it is not identical to that typically found on roofs, and the toxicity can vary significantly from one strain of algae to another. For this reason, the authors' company conducted both laboratory and field studies on the specific strain of Gloeocapsa found on roofs. Field study results from exposure panels in the Houston area have demonstrated superior performance by copper compared to zinc in the prevention of Gloeocapsa. Moreover, copper has the additional benefit of not resulting in the formation of white metal oxide layers on the shingle surface, as occurs with zinc. For these reasons, it was determined that copper was the material of choice around which to design an algae-resistant roofing granule.

Another important issue that had to be resolved was how to best attach and distribute the copper on the shingle. Clearly, it is important that the presence of the copper be as unobtrusive as possible, and it must provide adequate protection over the entire roof. Two distinctly different methods were considered: the concentrated placement of the copper in a strip just below the headlap and a uniform distribution of the copper throughout the exposed portion of the shingle. The strip application has the advantage of being an easy way to apply the copper granules to the shingle; however, studies indicated the effectiveness of this method to be significantly less than the second. The second method, a uniform distribution application, allows for an optimized performance by minimizing the granules' reliance on the "wash-down" effect, which is water carrying sufficient concentrations of copper ions down the roof to prevent algae growth. Although this does occur, as observed by the clean areas beneath metal vent pipes, it is believed that this can only be effective if relatively high concentrations of copper are present at the top of the wash-down, compared to that really needed to inhibit growth. To do this for an entire roof would be prohibitively expensive, not to mention wasteful. In addition, wash-down can be severely limited in the relatively stagnate moisture from dew. This is important for a couple of reasons: 1) dew provides ample water for the growth of algae and 2) dew can often be present on roofs for up to 12 hours a day. As mentioned earlier, in order for the copper to be effective at preventing algae growth, it must be present on the roof as aqueous cupric ions. In fact, it is believed that dew is the most critical source of water for the solubilizing of the cuprous oxide. Rainwater will surely result in leaching of copper, as well; however, the majority of the rainwater will run off of the roof much too quickly for any significant amount of leaching to occur. Furthermore, dew is present a vast many days, whereas rainfall generally occurs less frequently. Therefore, it is critical that the algae-resistant system ensure that cupric ions are present in the dew across the entire roof.

This then lead to the development of a roofing granule that contains a leachable source of cuprous oxide in the ceramic coating. This copper granule is designed around the same base rock as standard color granules. The base rock is first coated with a ceramic overcoat containing cuprous oxide. This is followed with a patented seal coat that provides a controlled, consistent leach of the copper onto the roof surface.[12] This outer coating also allows for the production of several different colors of copper granules so that it can fit in with various blend patterns. This granule, when uniformly blended with the traditional color granules, provides a sufficiently consistent copper ion release across the shingle. The key to the success of this type of system relies on an understanding of the leach rate of the copper in the coating and the level at which these copper granules need to be blended with standard color granules in order to ensure a sufficient level of cupric ions in the dew at all points on a roof surface. To efficiently gain this understanding, the leach performance of the copper granule was mathematically modeled.

MODELING OF THE COPPER GRANULE

Before beginning to model the leach performance of the copper granule, it was necessary to understand the dominant mechanism resulting in the release of copper. As presented above, dew was assumed to be the most important source of water for the leaching of copper on the roof. This lead to the theory that the dominant mechanism for the distribution of copper ions on the roof is from leaching into dew and residual moisture left on the roof after a rain shower. Because algal cells aren't killed instantly on contact with copper ions but are poisoned over time, it is essential that the solubilized copper is present on the roof at least long enough to interact with any algal cells. This is important in preventing cells from becoming established on the shingle surface. Therefore, the modeling work is based on the assumption that moisture from dew provides the dominant means of copper leaching.

The authors' approach to modeling the leach performance of the copper granule is based on a finite element analysis around the mass flux equation for the copper granule. Furthermore, because the granule was specifically designed with an outer seal coat that provides controlled release of the copper initially bound in the inner ceramic matrix, it was determined that diffusion of the cupric ions through the seal coat is the limiting step in the leach mechanism. Finally, the seal coating on the granule was approximated as a spherical shell as shown in Figure 1.[12]

Looking at the copper granule from a fundamental mass balance basis, each granule contains a finite mass of copper oxide that is depleted at a time-dependent leach rate. This mass flux equation can be written for any given time as:

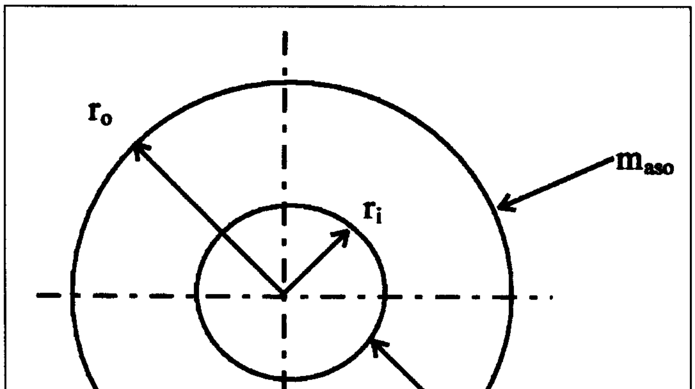

Figure 1. Spherical shell model of copper-coated granule.

Mass Remaining=Initial Mass-Mass Leached

$$M(t)=M_o-\int_0^t C(t)dt \qquad [1]$$

where $C(t)$ is the time-dependent leach rate that is integrated over time to give a mass of copper leached. Equation 1 can then be rewritten in the differential form, and the spherical shell description (see Figure 1) can be applied to the variable C:

$$-\frac{dM}{dt}=C \qquad [2]$$

$$C=\frac{M_{asi}-M_{aso}}{\frac{1}{4\pi\rho D_{AB}}\left(\frac{1}{r_i}-\frac{1}{r_o}\right)} \qquad [3]$$

where M_{asi} and M_{aso} are the mass fractions of copper at the inner and outer surfaces of the seal coating, D_{AB} is the diffusion coefficient of copper ions in the seal coat, ri is the radius to inner surface of the seal coat, and r_o is the radius to outer surface of the seal coat.

By assuming that the mass fraction at the outer surface, M_{aso}, is essentially zero and defining the physical constants in C into a single term, C^*, the differential leach expression can be simplified:

$$\frac{dM}{dt}=\frac{M(t)}{C^*} \qquad [4]$$

where C^* is a factor relating to the diffusion coefficient of copper ions through the seal coat, the effective thickness of the seal coat, and granule mass and density.[12] Simply integrating and solving this expression for the time-dependent mass term results in Equation 5.

$$M(t)+M_o exp\left(\frac{-t}{C^*}\right) \qquad [5]$$

From this equation, leach curves showing the amount of copper remaining in the system vs. time can be generated as shown in Figures 2 and 3.

Figure 2 shows the correlation of the theoretical leach predictions from the model with actual experimental leach results from real-time exposure of the copper granules in the Houston, Texas, area. The real-time leach data is obtained from

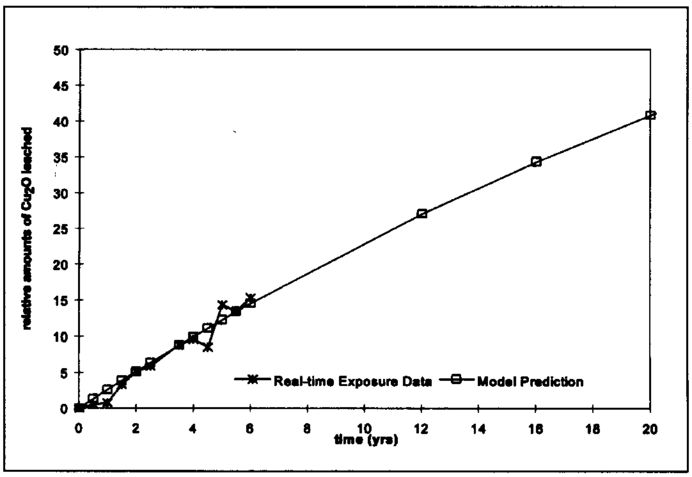

Figure 2. Comparison of model leach predictions to actual exposure data from Houston, Texas, with a 45-degree pitch.

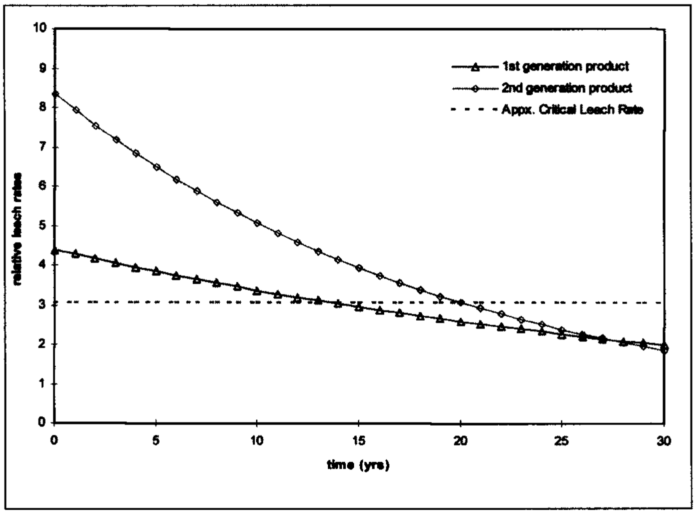

Figure 3. *Comparison of predicted relative leach rates between original and optimized copper granules. Curves are based on a 10 percent blend of copper granules with standard color granules. The critical leach rate is based on the minimum necessary copper ion concentration required on the roof to inhibit growth.*

x-ray fluorescence measurements of the amount of copper remaining on the exposure panels every six months. The difference in the amount of copper from the previous measurement is the amount leached in that time period. Care is taken to obtain a statistical number of measurements each time to help account for any variability on the shingles. The excellent correlation of theoretical to actual results achieved continues to verify the applicability of the model to this system. Additionally, this correlation has provided the confidence to use model predictions in understanding the long-term performance. In fact, model-generated leach data has proven very useful in optimizing the design of the copper granule.

Figure 3 shows how the modeling of leach performance leads to greatly improved product performance in terms of the estimated algae-resistant lifetime. Both products modeled in Figure 3 contain the same initial mass of copper oxide, but by using model results to determine optimum leach rates, the authors were able to make more effective use of this copper. This resulted in the commercial introduction of the second-generation product.

As with all modeling work, especially that involving long-range predictions, there is a fair amount of error and uncertainty that is inherently present in the results. For this reason, relative comparisons are much more useful than predictions of absolute performance values. Therefore, the values listed on the time axis were included for comparative convenience and should not be taken as absolute lifetimes. However, as mentioned above, the authors have demonstrated that up through six years, this time scale does match actual performance quite well, and they continue to track model predictions in this manner.

Another important consideration influencing prediction of an absolute algae-resistant lifetime is the uncertainty in pinpointing an exact minimum level of copper needed to completely inhibit algae growth. The value of 0.5 PPM copper has been estimated for use in Figure 3 (represented by the dashed line on the figure) from literature data as the toxicity of copper towards aquatic algae.[13, 14] Ongoing joint research between the authors' company and a university has indicated that the critical copper concentration may actually be higher for some cultures of Gloeocapsa and Scytonema taken from the roof environment. Because of the exponential shape of these curves, relatively small shifts in this minimum required copper concentration will have a significant effect on the estimated lifetime. The authors' modeling work (Equation 5) led to the determination that a 10 percent uniform blend of copper granules with standard color granules is necessary to ensure a minimum of 10 years of algae resistance given the current degree of accuracy in model parameters. Continued efforts to refine these parameters and improve the model accuracy emphasizes the importance of algae research, such as the determination of more accurate critical copper ion concentrations for the inhibition of the specific strains of algae commonly found on roofs. One final note is that these copper-coated granules are designed around the same base rock as standard roofing granules and contain a pigmented color coat; they will continue to provide UV protection to the asphalt shingle regardless of the amount of copper that has been leached out.

CONCLUSIONS

This paper presented research identifying the specific types of algae most commonly found to be the cause of roof discoloration. A nationwide survey of roofs identified these algae as the Cyanobacteria, Gloeocapsa, and Scytonema. Investigation into the characteristics of these algae revealed that they are quite well-adapted to the Spartan roof environment. These algae are capable of obtaining much of their nutritional requirements through photosynthesis and fixing nitrogen from the air. The dark nature of the Gloeocapsa is, in fact, due to a pigment in the cells that is generated as a protective response to UV radiation exposure.

A brief review of literature on a proposed mechanism by which metal ions, such as copper and zinc, inhibit the growth of roof algae was presented. Based on a ranking of the relative effectiveness of various metals in preventing algae growth, copper was determined to be the best metal to use in the design of an algae-resistant granule.

Different means of attaching and ensuring adequate delivery of the copper to the entire roof surface were explored. It was found that the copper is best attached to the shingle as part of a ceramic coating on the roofing granule. Control of the rate of delivery of cupric ions and the final color of the copper granule are determined by a patented outer seal coat around the granule. A uniformly blended application of at least 10 percent copper granules with standard color granules is necessary to ensure consistent delivery of the copper ions to the entire roof. This is based on the identification of dew as the dominant source of water for the leaching of copper.

Finally, a finite element analysis was used to develop a mathematical model that can be used to simulate the real-time leach performance of the algae-resistant, copper-containing granule. Excellent correlation of the model results to real-time exposure results has been obtained. Building on this, the model has been used to optimize the copper granule. The result is an algae-resistant, copper-containing granule with a significantly improved effective lifetime compared to the first-generation copper granule product, which used the same initial amount of copper oxide.

The ability to generate relatively realistic theoretical leach profiles for this copper granule provides significant insight into actual performance on the roof. This insight and understanding of the algae problem and solution is critical in meeting the authors' objective of providing a high-quality roofing product. As roof algae continues to become a more and more widespread problem, homeowners are asking for an explanation of the resulting discoloration. This article presents insight on this problem and provides a reliable, proven solution to roof algae discoloration.

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