Ultra-slow Release of Trifluralin from Polymers

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Abstract

Slow release of trifluralin to inhibit root intrusion into drip irrigation emitters is a well-known technology. Ultra-slow release to double the expected life of such products, has recently been developed.

The concept is based on the recognition that nanometer sized inert inorganic particles, such as nanometer sized clay particles, can be incorporated into a polymeric host carrier, in order to control the diffusion rate of a dispersed slow-release material. The active slow-release material may comprise a bioactive chemical such as a fungicide, bactericide, insecticide or herbicide. The presence of the nano-clay particles reduces the porosity of the polymer, or otherwise obstructs the diffusion of the active material being released, thereby increasing the length of the path of the diffusion through the host polymer. This further slows the rate of release of the slow-release material. The method of blending the materials proves to be critical.

Introduction

There are products in the marketplace that depend upon slow-release technology. One product slowly releases a herbicide from a polymer into soil in order to inhibit root intrusion into that area (Burton et. al. 1992). Flea repellent dog collars are another example where an insecticide is slowly released from the polymer in the collar. In many cases more of the active material is released than is necessary to efficiently meet the product requirements. In other words, a lower rate of diffusion through the polymer would result in a longer effective product life.

The application discussed in this paper is a drip irrigation device that inhibits root intrusion by incorporating trifluralin (an herbicide) into the drip emitter. This technology has been successful in protecting buried drip irrigation devices from root penetration for periods of more than fifteen years. The herbicide is incorporated into a polymer matrix, which protects the trifluralin from chemical or biological degradation. This simultaneously provides a controlled, sustained release of the herbicide to the soil adjacent the device. The blending of a nano-clay into the polymer can extend the expected life of the herbicide by as much as 90%.

Materials and Methods

An intercalation material comprised of an inert fine particulate inorganic material with a layered structure (a nano-clay) is incorporated into a mixture of the slow-release bioactive material and the host polymer. The slow-release material is accommodated within spaces between the layers of the intercalation material to slow the diffusion rate of the slow-release material through the host polymer, as compared to the diffusion rate of the same slow-release material through the same host polymer not containing the dispersed intercalation material. The intercalation material is surface-treated to expand the spaces between the platelets that form the dispersed material. The active material is released at a controlled reduced rate, but at a level sufficient to maintain its effectiveness, while the resinous carrier maintains its structural properties.

The nano-clay is a montmorillonite, an alumino-silicate. The particles are in layered form, i.e., formed as platelets. These particles measure on the order of one micron (0.00004 inches) in diameter and a thickness of about 0.001 micron (or one nanometer), giving them an aspect ratio of about 1,000:1. Relatively small amounts of nanometer-sized clay particles, approximately 2% to approximately 10% by weight, are dispersed in the resinous matrix formed by the host polymer and the dispersed active material. The use of nano-clay materials to reinforce the mechanical properties of plastic materials such as nylons and polyolefins is described in by Sherman (Sherman, 1999).

Three masterbatches were prepared.

“Mix” refers to a simple mechanical mixing without the application of heat or shear. “Compound” refers to mixing under heat and shear, followed by pelletizing, in order to produce nearly homogeneous granules.

“MBN” is the nano-clay masterbatch. Nano-clay is compounded in a polyethylene resin in the ratio of 40:60. Intercalation techniques similar to those described in the Qian (Qian et. al., 2001) were used for surface treating the nano-clay particles with a surface modifier to expand the spacing between platelets. Polyethylene resin was mixed with the clay particles to form a co-intercalate material

MBT is the trifluralin masterbatch. The trifluralin-containing material was made of 50% polyethylene resin, 25% trifluralin, and 25% carbon black. These components were blended and then compounded in a twin screw compounding extruder into a masterbatch according to techniques disclosed in Burton (Burton, et. al. 1992).

MBTN is the combined masterbatch. The component materials for MBT were mixed together, but not compounded. MBN was added. The ratio of materials was: polyethylene 30%, trifluralin 15%, carbon black 15% and MBN 40%. The resulting mix was compounded in a twin screw compounding extruder.

For the first experiment, two mixes were prepared. MBT was mixed with linear-low density polyethylene (LLDPE) in the ratio of 75:25. And, MBTN was mixed with LLDPE in the ratio of 58.33:41.67. Both mixes contained 6.25% of trifluralin.

For the second experiment, the MBN and MBT masterbatches were mixed to produce the following three mixes:

TABLE 1

	1	2	3
MBN	0.00	12.49	24.98
LLDPE	75.02	62.53	50.04
MBT	24.98	24.98	24.98
Total	100.00	100.00	100.00
(MBN/MBT)%	0%	50%	100%

In both experiments, the mixes were injection molded to form drippers. Four drippers in each set were placed in an aluminum foil dish and weighed. Initial weight of the drippers was 16 gm. They were then placed in an oven, using a slow extraction fan to remove the trifluralin as it left the drippers. The first experiment was conducted at 56.67º C (134º F.); and the second experiment at 88.90º C. (192º F.) In order to observe the extraction rate, the samples were weighed periodically over until the rate of extraction leveled off and the majority of the trifluralin contained in the parts had been lost.

Results and Discussion

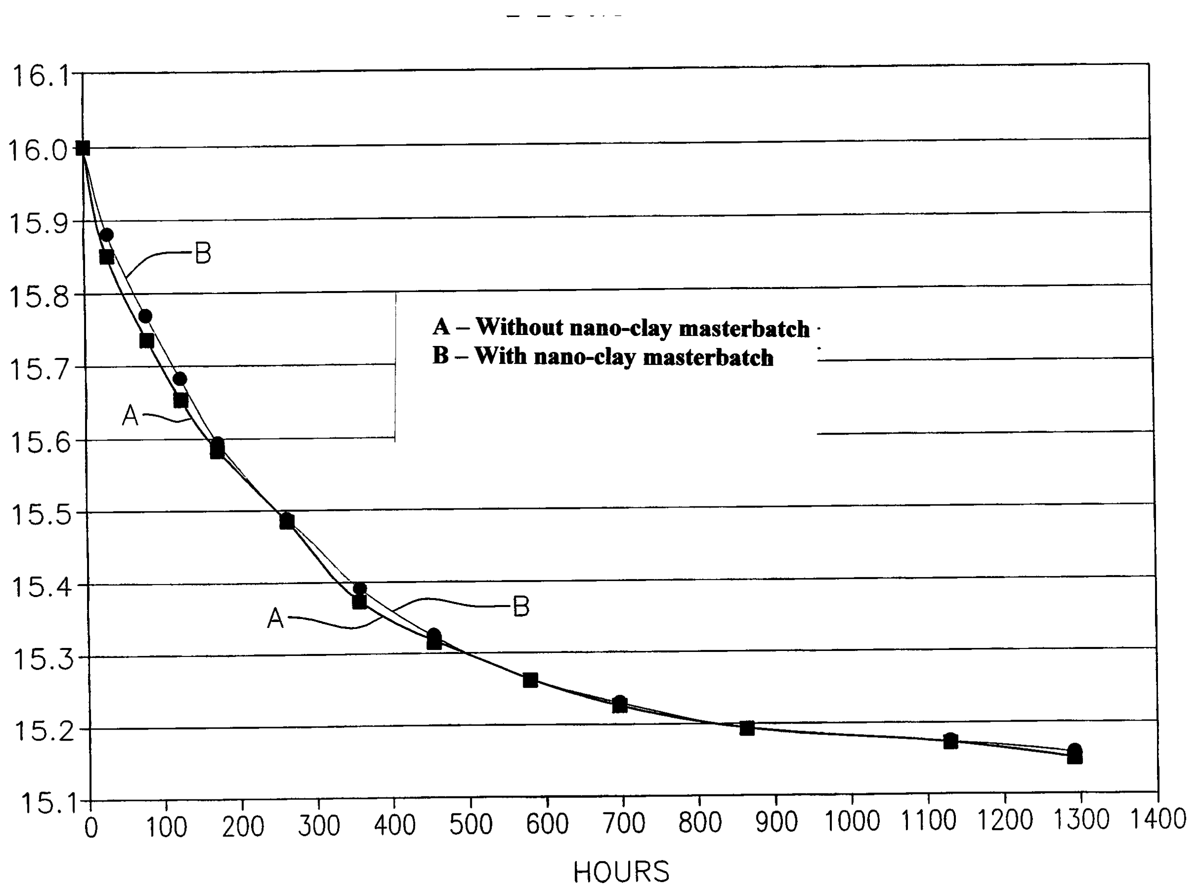

Figure 1: MBT and MBTN. Loss of weight in gms. against time in hours.

The first experiment: The graph shown in FIG. 1 illustrates the extraction rate of trifluralin from the drippers. The data shows that extraction rate (or release rate) of trifluralin from the drippers is not effected by the presence of the nano-clay. This result was most disappointing. The project was dropped for six months.

The second experiment: The graph shown in FIG. 2 illustrates the extraction rate of trifluralin from the drippers molded from the mixes shown in Table 1. The data shows that extraction rate (or release rate) of trifluralin from the drippers progressively decreases with a proportionate increase in the level of nano-clay contained in the dripper body.

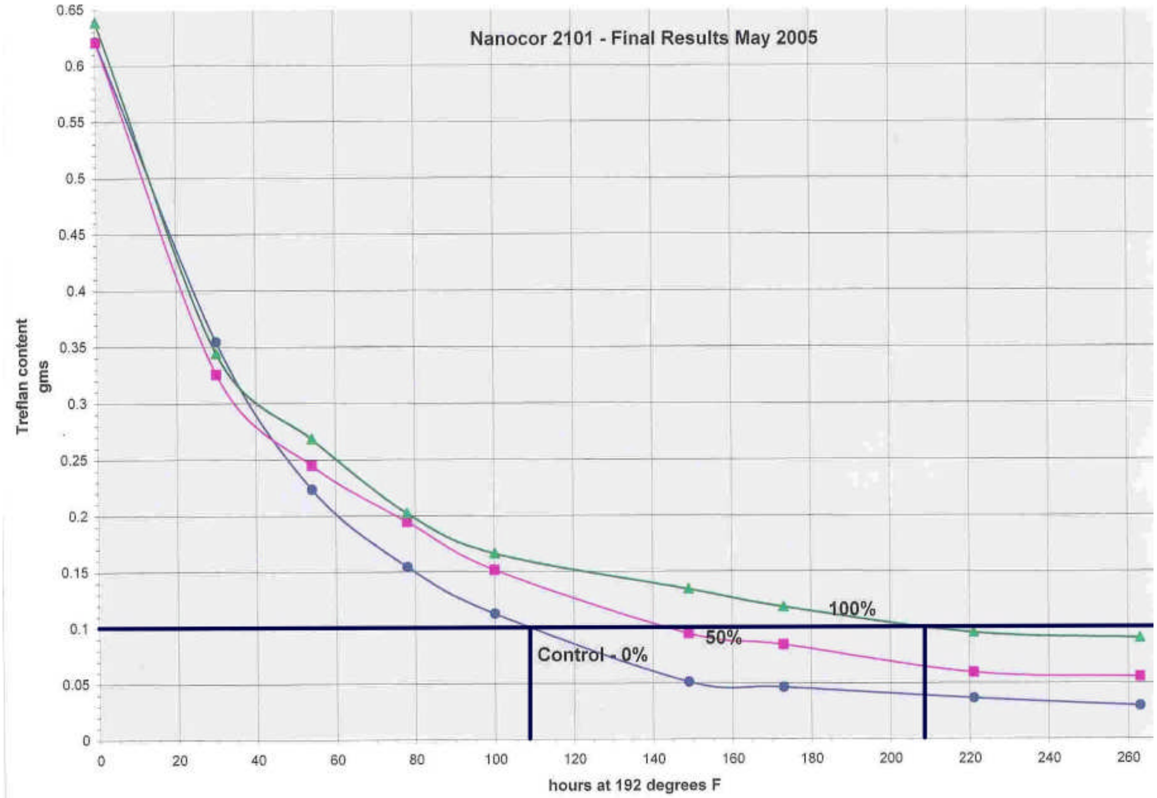

Figure 2: Reduced rate of loss of weight with increase concentration of nano-clay – MBN

More specifically, from Fig. 2, the time for the remaining concentration of trifluralin to drop to 0.1 gms is:

Control	109 hours
50%	145 hours - 41% increase
100%	209 hours - 92% increase

Apparently, the bond of the trifluralin with the carbon black is so strong that in the first experiment, adding the nano-clay did not decrease the rate of release; however, by adding the two masterbatches separately, the rate of diffusion from the carbon black was reduced by the barrier of the nano-clay in the LLDPE carrier.

It is believed that the process of utilizing dispersed nano-clays for slowing the diffusion rate of the active material from the polymeric carrier is caused by the phenomenon known as "intercalation." Intercalation compounds are formed when the "guest" molecule, in this case trifluralin, can be accommodated in the spaces between adjacent layers of the "host" molecule, in this case, the montmorillonite. Over time, trifluralin will diffuse out of the clay particles and the polymer at a rate that is slower than the release rate from a similar structure not containing the nano-clay particles. Such layered, inert, inorganic, fine particulate materials which are effective in controlling slow-release active materials, such as bioactive chemicals or herbicides, to slow their release rates are referred to as "intercalation materials." The phenomenon known as "intercalation" is described in "Preparation of inorganic - organic nanocomposites by intercalation and its application to materials," published by *Applied Chemistry*.

Conclusions

The data above shows that the addition of a nano-clay, in the manner described, is effective because the addition of 10% of a nano-clay resulted in a 92% increase in the time to loose approximately 83% of the trifluralin incorporated into the molded dripper. This, of course, means that there will be an equivalent increase in the effective life.

This paper claims that the manufacture of two separate masterbatches is essential, and that combining the manufacture of the masterbatches into one single masterbatch does not result in any slow-down of the release process.

This process can be applied to many slow release applications, such as termite barriers, fertilizers, anti-graffiti paint etc. (Ruskin 2004).

Further Research

Following the argument above, it is possible that by first compounding the MBN with all the LLDPE to get the desired concentration, and then adding the MBT, an even slower release rate could be produced.

Literature Cited

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