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PROPOSED PREPARATIVE TECHNIQUES FOR
MANUFACTURE OF MARINE DYE MARKER

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Proposed Preparative Techniques for Manufacture of Marine Dye Marker

R.J. Swinton and R. Gray

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Abstract

A marine dye marker has been developed at MRL. Favourable publicity and interest from sea safety authorities make it likely the marker will be produced on a large scale. It will be marketed under the brand names "Seamark" and "Lifemark".

This report reviews the laboratory scale manufacture and discusses its shortcomings. Techniques for large scale production are investigated and two are found to be suitable. These are based on pelletizing and granulating technology and both require slight changes to the original formulation.

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Contents

1. INTRODUCTION	5
2. DESCRIPTION OF DYE MARKER	6
2.1 Concept	6
2.2 Description of Fluorescein	6
2.3 Current Method of Dye-marker Manufacture	6
3. STUDY OF PRODUCTION TECHNIQUES	7
3.1 Pelletizing	8
3.1.1 Mixing	8
3.1.2 Extrusion	8
3.1.3 Drying	8
3.2 Granulating	8
3.2.1 Binder	10
3.2.2 Drying	10
4. QUALITATIVE TESTS	10
4.1 Air Drop Test	10
4.2 Structural Strength Test	11
4.3 Time to Dissolve Test	11
4.4 Dispersion Test	13
4.5 Effect of Moisture	13
5. CONCLUSIONS	13
6. ACKNOWLEDGEMENT	16
7. REFERENCES	16

Proposed Preparative Techniques for Manufacture of Marine Dye Marker

1. Introduction

An innovative search and rescue, marine dye marker has been developed at Materials Research Laboratory (MRL) Melbourne [1]. The marker contains the fluorescent dye, fluorescein, in a buoyant slow-dissolving matrix. When deployed on the sea surface, dye from the marker permeates the water, creating a highly visible signal of long duration suitable for detection by both aerial and surface rescue craft.

Successful demonstrations of the vast improvement over existing commercially available dye markers has meant that a number of devices, not previously feasible, are now potentially marketable [2]. These include boat-packs (for pleasure craft and life rafts), capsules (for attachment to life jackets), scuba-diver capsules and fixed wing and helicopter aerial deployment packs.

Prior to the demonstration of the MRL marker in the Great Barrier Reef Marine Park, north Queensland, the widely held belief was that fluorescein dye markers were of little value as a rescue aid in aquamarine coloured tropical waters. It was shown that this was true of commercially available dye markers but the MRL marker was described [2] as "performing brilliantly".

The new dye marker was patented under Provisional Application No. PJ 2905, and a manufacturer found to make under licence and market the various devices.

To make this licensing agreement even more commercially attractive, the manufacturing technique has been re-examined with a view to large scale production.

2. Description of Dye Marker

2.1 Concept

The MRL dye marker combines two simple ideas. It keeps the dye on the water surface by bonding in onto super-light polyvinylidene chloride (PVDC) microspheres and it controls the rate of dissolution by using a slow-dissolving water soluble binder gum.

The marker was first designed as a component of a submarine location marker [3]. It was observed during this development that conventional fluorescein dye markers had two major drawbacks. They are slow to activate, and they dissipate rapidly. Fluorescein dye has a density of approximately 1.5 Mg/m³ and when bulk dye is dissolved at the surface of deep water, dissolving dye pieces sink and fluorescence is diminished.

The product recommended for use in the submarine location marker was very efficient and therefore small amounts could achieve the required size distinctive surface mark [4].

2.2 Description of Fluorescein

Fluorescein is the common name for the disodium salt sea marking dye, often used in devices such as life vests and life rafts. Its scientific nomenclature is disodium 6-hydroxy-3-oxo-9-xanthene-o-benzoate. It is described in the Colour Index [5] as CI Acid Yellow 73, Constitution No. 45350.

Fluorescein, disodium salt is marketed under various chemical names — Fluorescein LT (ICI), Uranin, Basacid Yellow 226 (BASF) — and costs about \$54/kg. A comparison of the spectra of equal concentrations of both ICI and BASF brands showed that the latter gave a clearly superior colour output (Fig. 1). In the early stages of product development the ICI LT brand dye was used as a large stock was available at MRL.

2.3 Current Method of Dye-marker Manufacture

The first step is to prepare the sodium carboxymethyl cellulose (SCMC) synthetic gum which is used to bind the dye to the microballoon surface. This is accomplished by pre-wetting Diacel 1130 brand SCMC with ethanol, then whilst heating and stirring, adding sufficient water to completely dissolve all the gum. Heating is then continued until both all the ethanol has been removed (evaporated) and the mixture has attained a clear pourable gelatinous consistency. It is important to remove the pre-wetting solution as the PVDC microballoons are ethanol soluble. This is best achieved by boiling the mixture for one hour. Glycerol is then added to the hot mixture.

Secondly, the dry ingredients (fluorescein and microballoons) are blended together in a planetary-action mixer. The binder solution is then slowly added, with stirring, until a pliable, putty-like consistency is attained.

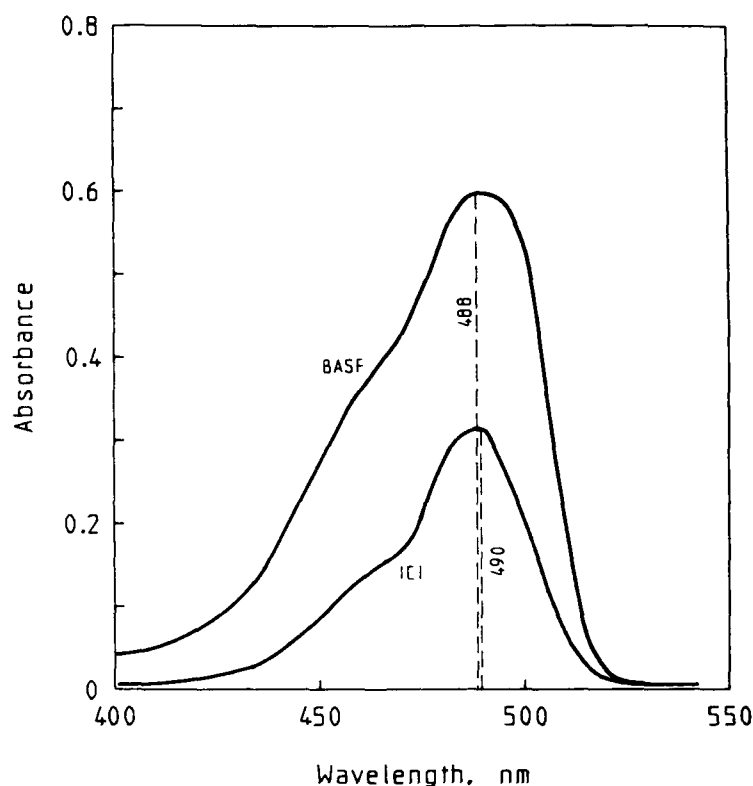


Figure 1: Visible spectroscopy of equal concentrations of BASF brand and ICI brand fluorescein dyes.

While the mixture is still warm it is poured into trays and dried. The drying process was found to require two separate stages of oven heating: 40–45°C for 72 hours then 95–100°C for 24 hours. The lengthy dual drying process is necessary to prevent the formation of a hard surface crust. Such crusts were observed to form blisters containing entrapped water.

3. Study of Production Techniques

The prolonged drying and manual breaking of the dried cake into flake pieces is inefficient for large scale production. As a result, an investigation was undertaken to assess other more suitable production techniques.

3.1 Pelletizing

A pelletizing process was developed which necessitated a formulation modification. It was necessary to include both bulking (fumed silica) and film producing (glycerol) agents to facilitate retention of the extruded shape. The percentage of ingredients were adjusted such that the dried pellets would have the same density as the flake material.

3.1.1 Mixing

As in the flake configuration the binder used to hold the dye to the microballoon surface was Diacel 1130. The rate at which the binder and therefore the pellets dissolve in seawater is regulated by the degree of substitution of polar groups (in this case, carboxymethyl) to the normally insoluble long chain cellulose molecule [6].

The same procedure as described earlier (Section 2.4) for the flake form was used to prepare the binder solution.

The dry ingredients (fluorescein, microballoons and fumed silica) were again mixed in a planetary type mixer until a uniform consistency was obtained. The binder was then slowly added, with continuous stirring, until a pliable putty-like consistency was attained.

3.1.2 Extrusion

The resultant mixture was loaded into the chamber of a pneumatic caulking gun and forced out of the 6 mm diameter aperture by a ram pressure of 0.5 MPa. This gave a smooth, steady extrusion rate of approximately 0.5 m/min. Lines of the material were extruded, in a continuous looping motion, onto Teflon coated plastic mats.

3.1.3 Drying

The cords of material were allowed to air dry for 24 hours before being removed from the mats and placed in an oven at 90°C for a further 24 hours. The dried cords were then removed from the oven and cut into pellets of the required size.

3.2 Granulating

A granulating technique using a Sprout-Waldron M400 rotating disc (40 cm diameter) granulator was also evaluated.

Basically the machine works on the rolling snowball principle, having a tilted rotating disk-drum in which the pre-mixed fine dry sample is caused to tumble under centrifugal force around the disk while a set of scrapers maintains a layer of uniform thickness. The process is shown schematically in Figure 2. A fine spray of the pre-mixed Diacel is focussed upon the tumbling sample causing

nucleus or seed granules to form. Growth is accomplished by the continuous layering of fines and liquid binder solution on the rolling bed of sample. The action of the disk separates fine sample, small granules, growing granules and the finished product into distinct areas within the disk. The placement of the liquid and solid feeds was found to largely determine the size of the agglomerates. Increasing the amount of solids fed into area III of Figure 2 led to the formation of more seeds or small granules, and thus kept the average granule size low. Introducing the solid feed into areas I and II led to fewer seeds, and larger granules. The angle of tilt and speed of rotation were used to optimize the pellet sizes; an angle of tilt of 37° and a pan rotation speed of 30 r/min were found to give a pellet of consistent size.

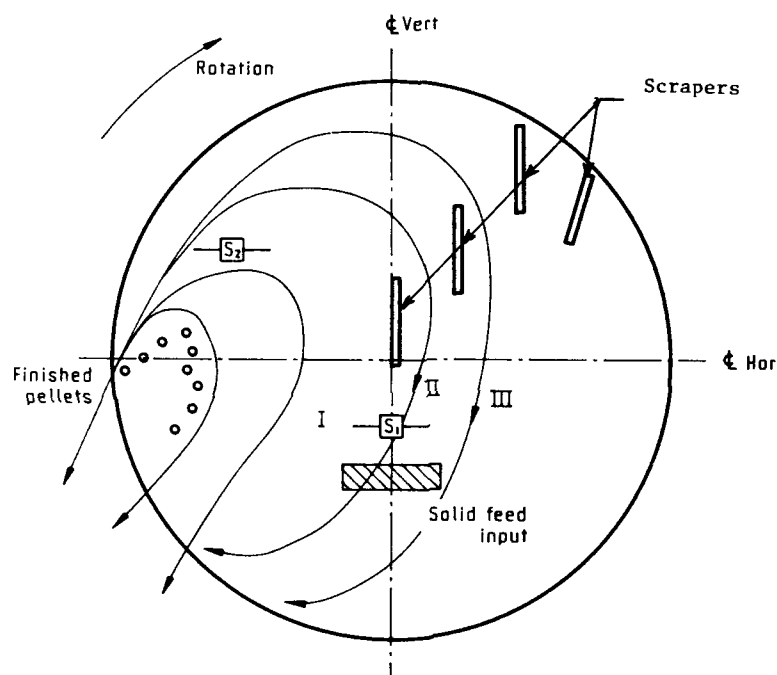


Figure 2: Example of set up and flow pattern of disk pelletizer. I. First Stream (final growth, densification, and polishing). II. Second Stream (intermediate growth). III. Third Stream (fines and seeds). S₁ Liquid spray location (primary). S₂ Liquid spray location (secondary).

3.2.1 Binder

The Diacel solution used as the binder in the granules needed to be less viscous to enable it to be sprayed through an atomizer. The solution was made by pre-wetting the Diacel with a small quantity of ethanol then dissolving in water (1 g/100 mL) and glycerol. Again all traces of ethanol were distilled off.

Approximately 400 mL of binder solution were used per 1 kg of dry mix to get the final semi-dry granules from the disc pelletizer.

3.2.2 Drying

During the tumbling processes the larger and drier granules tended to accumulate around the finished pellet area (area I of Figure 2). Increasing the angle of tilt of the pan caused agglomerates of the required size to roll over the rim of the pan where they were collected in a large flat tray. At this stage the granules, although appearing dry on the outside, still had the consistency and hardness of putty. When cured in an oven at a temperature above 60°C, moisture trapped inside migrated to the outer surface, causing granules to adhere to each other. This was overcome by hot air drying for approximately 1 hour before oven drying in a Qualtex electric fan forced oven. The granules were dried in their trays for 4 hours at 60°C and then a final 12 hours at 100°C, to remove all traces of moisture.

The finished granules need to be packaged immediately after drying, or kept in a dessicator, as they absorb moisture from the atmosphere more readily than the flake and pellet configurations.

4. Qualitative Tests

The following tests were used to assess the performance of the granules and extruded pellets produced against that of the original flake configuration. Pellets chosen for test were cylindrical in shape with a diameter of 6 mm and an approximate length of 10 mm. Granule diameters ranged from small (< 1 mm), medium (1-5 mm) to large (> 5 mm).

4.1 Air Drop Test

Each of the aerial drop-markers contained 100 g of dye marker material inside a water soluble polyvinyl acetate bag. The bags were dropped from a height of 50 m in a line running perpendicular to the direction of the tide. Granulated material was not tested here as the granulator had not yet been obtained.

Three samples were tested:

- A: original flake configuration;
- B: pelletized formulation in flake configuration;
- C: pelletized formulation in pellet form.

All were deployed from a helicopter into Port Phillip Bay about 30 m apart with approximately 2 seconds between each deployment.

Figures 3 and 4 illustrate the performance of the three samples, A, B, and C. From the test it was observed that the order of performance, after the following durations, was:

- 1 min - A best, B second, C third;
- 15 min - A best, B and C approximately equal;
- 30 min - A and C equal, B second.

This may not be immediately apparent when observing the photographs as the optical effect fluorescence has upon the eye is different from that of the camera lens. Order of performance was agreed upon by the crew of the Police helicopter (pilot, co-pilot and spotter) and both authors (who were aboard the helicopter).

It was deduced that the initial "blooms" observed from A and B were caused by the smaller, quicker dissolving particles of flake. This was considered to be a desirable feature for Seamark; it would be a simple procedure to incorporate a fixed ratio of fines and pellets to capture this effect consistently.

4.2 Structural Strength Test

Samples of both the extruded pellets and granules (100 g each) were individually placed inside a No. 10 BSS sieve and hand shaken for a duration of 5 min. There was little evidence of crumbling or dusting. When repeated for the original flake formulation, approximately 7% by mass passed through the aperture. Both the pelletizing and granulating processes can therefore be used to enhance the durability of the product after vibration and rough usage.

4.3 Time to Dissolve Test

A pellet of material was dropped into a 5 L water-filled container at 21 °C and stirred at approximately 50 r/min by a magnetic stirrer at the base of the container. The pellet hovered just below the water surface. The dye stain was observed to leach out of the pellet for a duration in excess of 1 hour.

The same test was repeated with a single granule of approximately 8 mm diameter. The granule floated just below the surface when stirred and was devoid of dye after 30 min.

When repeated for the flake configuration, a single flake was observed to emit dye for a duration of 1 hour. The dye marker pellets will produce a signal of longer duration than the dye marker granules, in rough or agitated water.

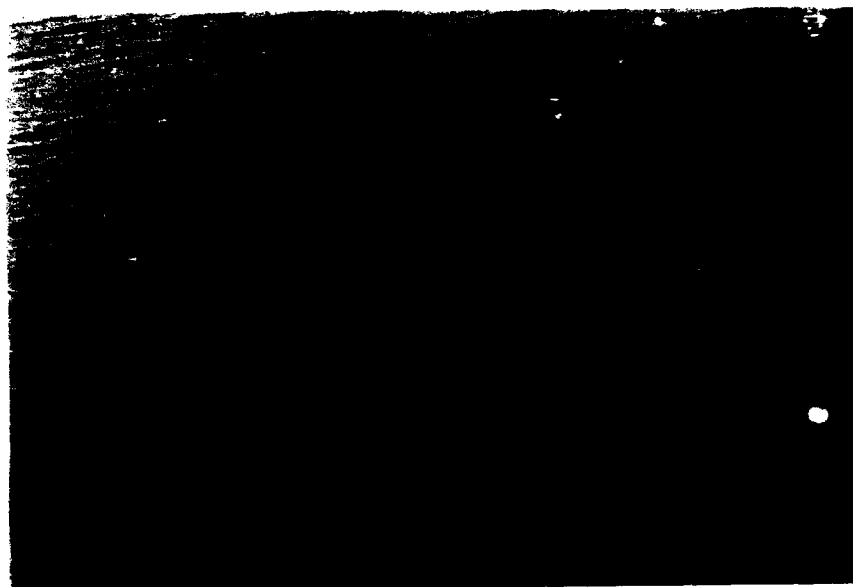


Figure 3: Signal after a duration of 1 min, taken from an altitude of 150 m.

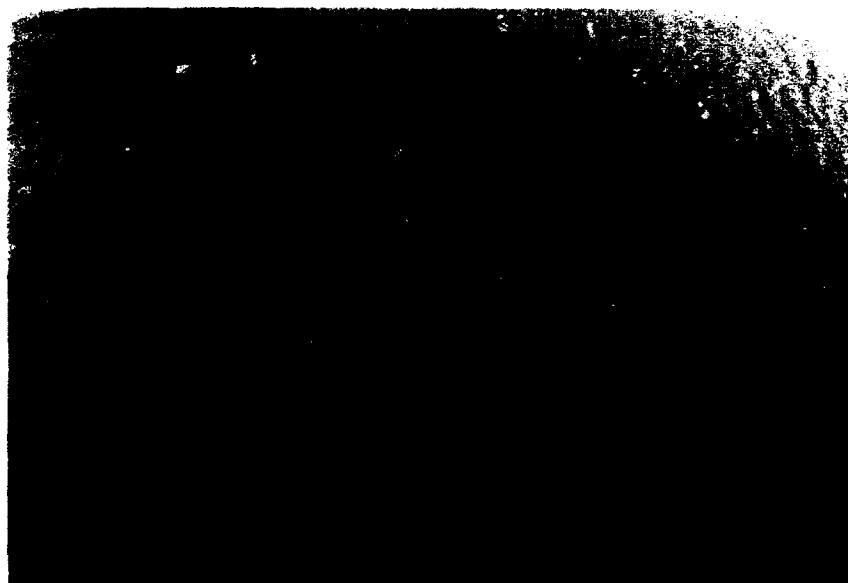


Figure 4: Signal after a duration of 15 min, taken from an altitude of 500 m.

4.4 Dispersion Test

The following 50 g samples were individually deployed from plastic containers of the type proposed for use aboard life-boats and pleasure craft [2]:

- A: flakes (original formulation);
- B: pellets (some crushed);
- C: granules (3-8 mm diameter);
- D: granules (1-2 mm diameter).

The seals were first torn free and the contents cast onto the water surface from the pier at Point Cook RAAF Base Laverton. Conditions were overcast with winds of 20-30 knots and choppy seas.

Dispersion of each sample was observed 1, 15 and 30 min after deployment, and performance was judged as follows:

- 1 min - D best, A and C approximately equal, B worst;
- 15 min - D best, A, B and C approximately equal;
- 30 min - D, A, C and B all approximately equal.

All the dye stains could still be seen after 30 min. Figures 5 to 8 show the performance of dye markers A to D at various times after deployment.

4.5 Effect of Moisture

It was observed during the trials at Point Cook that a small percentage of the dye marker sank to a depth of about 4 m and subsequently slowly rose to the surface. Since the containers had been left open for about 1 hour in the high humidity it was assumed that this was caused by moisture absorption. Further examination of samples A to D which were dried, weighed and left on the laboratory bench has shown an increase in weight from moisture absorption. It is probable that this moisture is replacing small entrapped air bubbles near the surface of the dye marker material tipping the fine balance between being barely buoyant to sinking. It is therefore important that the dye marker be kept in moisture proof containers.

5. Conclusions

Two potential methods of manufacturing the MRL dye marker on a production scale were investigated. Changes in the formulations were made to produce a dye marker which floated on or close to the surface.

Both the pellet and granule products give a visual signal comparable with the original laboratory scale flake method. Either method could be adapted for large scale manufacturing, with cost governing the final decision. Both processes can be used to produce a more structurally durable dye marker than the flake configuration.

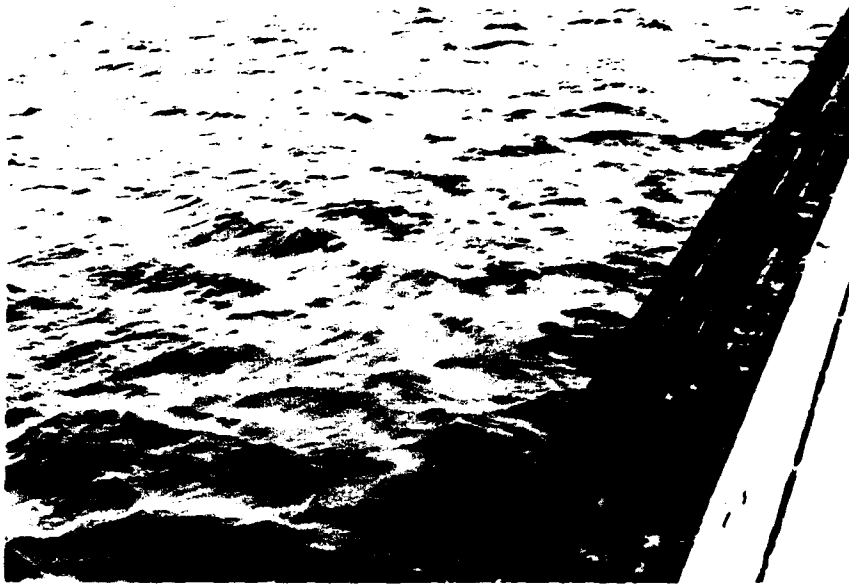


Figure 5: Signal from formulation A (30 min after deployment).

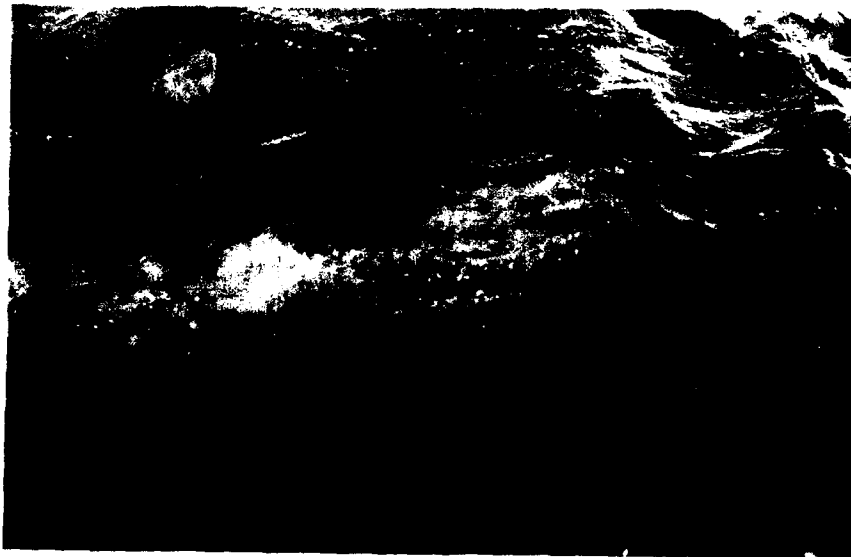


Figure 6: Signal from formulation B (10 min after deployment).



Figure 7: Signal from formulation C (immediately after deployment).



Figure 8: Signal from formulation B (5 min after deployment).

The pellet dye marker tends to result in a mark of longer duration and hence would be more suitable for boat packs and aerial deployment. The granule marker produces a more rapid deployment of the dye signal and hence may be more suitable for deployment from lifejackets.

6. Acknowledgement

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