

TECHNICAL NOTE

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SUMMARY

Colourants used as dye markers may allow the better targeting of pesticide sprays, and could help to protect operators, as well as reducing overall levels of pesticide use in forestry. Where a colourant is required, and where existing specialist pesticide marker dyes are unsuitable, the addition of 1.6 kg a.i. ha⁻¹ of the food dye Acid Blue 9 to the spray mix (e.g. through the use of 4 l ha⁻¹ Dysol Turquoise; 40% Acid Blue 9), is worth considering as a potential alternative. For post-plant insecticide sprays to the base of trees to protect against *Hylobius abietis*, a 0.8% dilution of the active ingredient Acid Blue 9 in the final spray volume (e.g. through the use of a 2% solution of Dysol Turquoise in the final spray volume) can give good results.

INTRODUCTION

Colourants have been used throughout history for a variety of purposes, and today form an essential component of industries as diverse as textiles, food, cosmetics and printing. Dyes are a form of colourant, soluble in solvent, which selectively absorb certain wavelengths or colours in white light. The colour seen by a human eye is determined by the wavelengths that are not absorbed by the dye, i.e. those wavelengths that are reflected or scattered by the compound.

The addition of dyes as markers in pesticides can help to:

- Improve the precision of applications, reducing the need for follow-up treatments and hence potentially reducing overall pesticide use and associated costs.
- Identify spray patterns, giving early indications of drift to non-target areas.
- Rapidly identify any faults in nozzles, sprayers and protective clothing, so reducing the likelihood of operator contamination.

However, potential disadvantages of dye markers are that they may be:

- Expensive.
- Harmful to operators and/or the environment.
- Difficult to handle, causing staining to skin and clothing.
- Capable of altering pesticide efficacy.
- Visually intrusive, which may cause concern among woodland users.

- Difficult to recognise by operators who are red/green colour blind (~ 8% of males and 0.5% of females).

Therefore the ideal characteristics of a colourant used as a dye marker in pesticide applications are for it to be cheap, soluble in water, safe to operators and the environment, have no effect on pesticide efficacy, and to be visible during spraying on a variety of sites and vegetation types, before fading to invisibility within a few days.

DYE MARKERS WITH POTENTIAL FOR FORESTRY USE

Some herbicides are already distinctively coloured, and do not require the addition of a dye marker. Commercially produced specialist pesticide dye markers are also available, some of which are specifically recommended for certain types of applications on herbicide product labels. These specialist pesticide dye markers can give good, economic results when relatively high concentrations of dye are used on small areas, for example with weed wipers, stump applications or post-plant insecticide treatment. However, they are often too expensive to use at rates that would make them visible in conventional low or medium volume herbicide spraying operations.

Numerous dyes have been developed for industries such as textile manufacturing, and many of these might be useful as cheap dye markers for pesticide applications. However, little is known about their visibility in forest conditions, or crucially their safety to operators or the wider environment.

EXPERIMENTAL WORK ON MARKER DYES

Because of the lack of available information on the subject, the Forestry Commission initiated a series of small-scale experiments with the aim of identifying potentially safe, cheap, alternative marker dyes. The experiments investigated a wide range of commercially available products, textile dyes and food and cosmetic dyes for their visibility, safety and effects on pesticide efficacy. The food dye Acid Blue 9 (Colour Index number 42090, available pre-diluted as the dye Dysol Turquoise, for example) was found to best fit the characteristics required for a pesticide marker dye. This work is reported in detail in the scientific paper by Brown *et al.* (2002).

CHARACTERISTICS OF ACID BLUE 9

Solubility

Acid Blue 9 is readily soluble in water, and is available pre-diluted as ready-to-use liquid dye.

Visibility

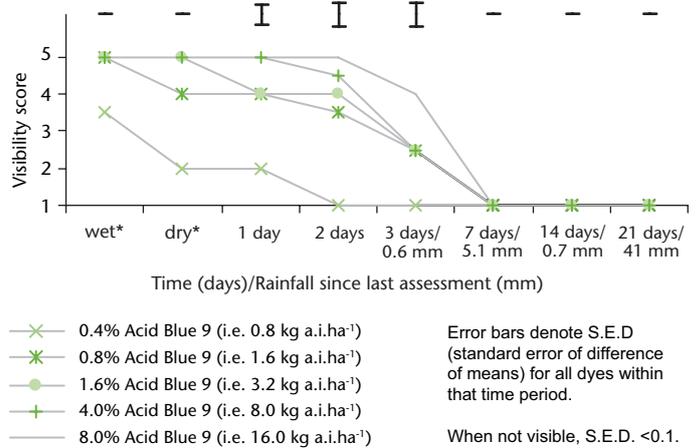
Figure 1 shows the visibility of Acid Blue 9, sprayed at concentrations ranging from 0.4–8% in 200 l ha⁻¹ diluent, in an experiment on herbaceous vegetation on a restock site. At concentrations of 0.8% or more, the dye was clearly visible immediately after spraying when wet or dry, but faded to invisible within 7 days and with 5.7 mm of rainfall. When the same treatments were applied to a restock site with bare ground, brash and dead vegetation, visibility was higher, and lasted longer, taking 21 days and 41 mm of rainfall to become invisible. Fading was probably due to be a combination of photodegradation, dilution, and some biodegradation.

Hence Acid Blue 9 at a concentration of 0.8% in 200 l ha⁻¹ diluent spray (equivalent to 1.6 kg active ingredient (a.i.) ha⁻¹ Acid Blue 9), will usually give a good balance between acceptable visibility on a variety of site types, and colour fade within a reasonable time period. However, in practice, visibility will depend on the amount of rainfall after spraying, vegetation type, dye concentration and individual perception (see Figures 3–6).

To increase the likelihood of persistent visibility for follow-up contract checking purposes, higher rates would be required (8 kg a.i. ha⁻¹ Acid Blue 9, or more), but this

Figure 1

Visibility of Acid Blue 9 used as a dilute spray on a restock site dominated by herbaceous vegetation (1 = invisible; 5 = clearly visible).



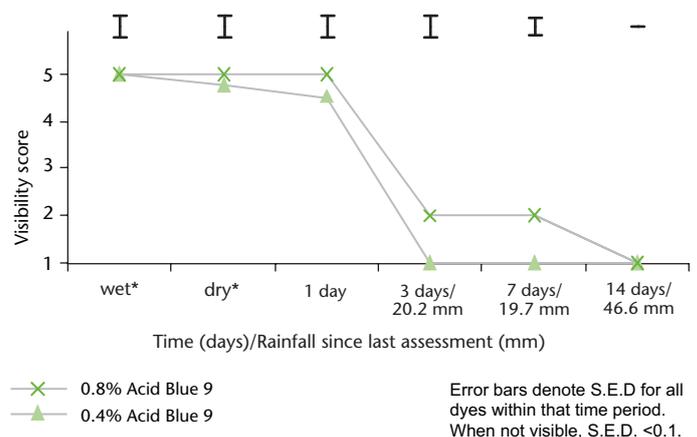
*Viewed immediately after application (no rainfall).

may affect pesticide efficacy. When using different diluent volume rates with the same amount of dye applied per hectare (1.6 kg a.i. ha⁻¹), although visibility on the ground should not vary greatly, with higher diluent rates visibility in sprayer tanks will be lower, as the actual concentration in the tank will be lower.

When tested as a post-plant insecticide spray – applied as two 10 ml sprays to the stems of Norway spruce (*Picea abies*), Acid Blue 9 was highly visible when wet and dry, but faded after 40 mm of rainfall (Figure 2). Acid Blue 9 at 0.8% of the final spray volume (i.e. a 0.8% concentration of Acid Blue 9 active ingredient in the water/pesticide mix) therefore gives good visibility for post-plant insecticide sprays to tree stems.

Figure 2

Visibility of two different dilutions of Acid Blue 9 dye used as top-up sprays on Norway spruce, scored on a scale from 1 = invisible, to 5 = clearly visible.



*Viewed immediately after application (no rainfall).

Figure 3

This application of 0.8% Acid Blue 9 is distinctly visible to the operator, and sprayer nozzle performance is also clear. However, at concentration rates that are economic to use, dyes may not always be visible for follow-up supervisory purposes.



Figure 4

Dye colour can appear to change as it dries, depending on the background colour of the material it is sprayed on. Here a 0.8% solution of Acid Blue 9, although originally blue when in liquid form, appears as a scarlet colour on green vegetation once dry. Brush and stumps however are stained blue.



Figure 5

The area on a tree stem sprayed with insecticide is clearly visible, due to the addition of Acid Blue 9 as a marker.

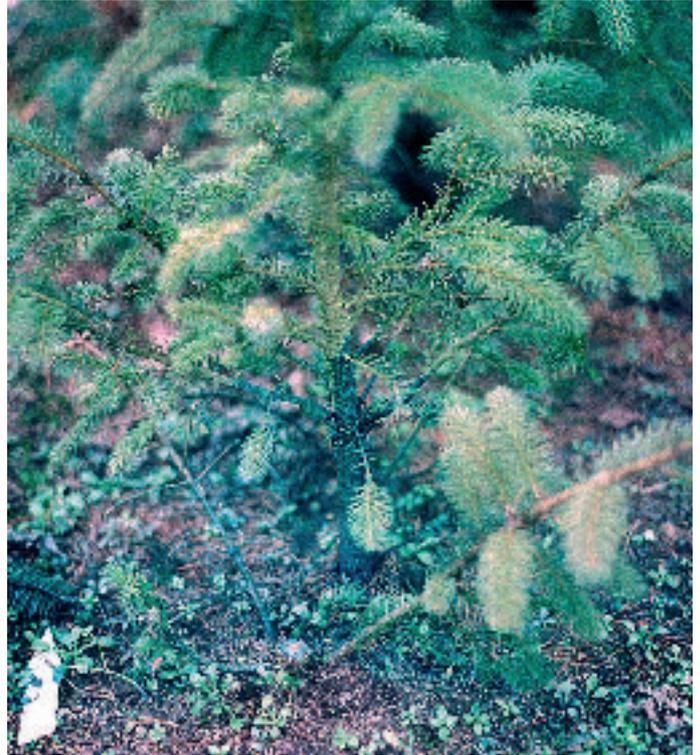


Figure 6

The visibility of dyes will vary depending on individual perception, vegetation type and the amount of degrade that has occurred since spraying due to sunlight, rainfall and biotic factors. Here, a 1.6% solution of Acid Blue 9 is moderately visible on young grass on the day of application, even after the spray solution has dried.



Efficacy

Experiments suggest that if relatively resistant weeds are treated, spray distribution is poor, or low rates of glyphosate are used on weeds that are difficult to control, then dyes such as Acid Blue 9 can reduce the efficacy of glyphosate, and possibly other foliar-acting herbicides such as asulam. Propyzamide, a soil-acting herbicide, appears to be unaffected.

In summary:

- Acid Blue 9 (at a rate of up to 2 kg a.i. ha⁻¹) is likely to be suitable for use with glyphosate where:
 - (a) Rates of 1.8 kg a.i. ha⁻¹ (equivalent to 5 l ha⁻¹ Roundup Pro Biactive, for example) or more are used, and;
 - (b) Weed species are normally well controlled by a single application of product, if applied using the appropriate method and rate as specified on the product label.
- Acid Blue 9 (at a rate of up to 2 kg a.i. ha⁻¹) is likely to be suitable for use with asulam where:
 - (a) Rates of 1.5 kg a.i. ha⁻¹ (equivalent to 3.75 l ha⁻¹ Asulox, for example) or more are used, and;
 - (b) Weed species are normally well controlled by a single application of product, if applied using the appropriate method and rate as specified on the product label.
- Acid Blue 9 (at a rate of up to 2 kg a.i. ha⁻¹) is likely to be suitable for use with propyzamide.
- For other herbicides, Acid Blue 9 (at a rate of up to 2 kg a.i. ha⁻¹) is likely to be suitable provided:
 - (a) Weed species are normally well controlled by a single application of product, if applied using the appropriate method and rate as specified on the product label, and;
 - (b) A small test application is made before large-scale, costly, or operationally critical applications take place.

Experiments also tested the effect of mixing dyes with the insecticides permethrin (Brown *et al.*, 2002) or alpha-cypermethrin (S. Heritage, pers. comm.). These have been

used in recent years as post-plant sprays on transplanted seedlings to reduce the incidence of damage from *Hylobius abietis*. Acid Blue 9 at 0.8% of final spray volume had no effect on the insecticides. Although its effect on cypermethrin or other possible future replacement insecticides for the control of *Hylobius abietis* is untested, based on these previous results, it is unlikely that Acid Blue 9 will have a negative impact on insecticide efficacy. Hence Acid Blue 9 is worth considering for use with post-plant insecticide sprays.

Safety

The Pesticides Safety Directorate advises that dyes used as markers are not covered by pesticide regulations. However, users intending to add marker dyes to pesticides must comply with the statutory conditions of approval of the pesticide product itself, and also ensure that the Control of Substances Hazardous to Health (COSHH) assessment and any control measures adopted take account of the dye used. Hence when using Acid Blue 9, a safety data sheet should be obtained for the specific formulation sold by the manufacturer, and a COSHH assessment carried out. Although not classified as a pesticide, or covered by the regulations, it is recommended that, as a minimum, the same routine operator and environmental precautions should be adopted as would be used for any pesticide.

Dye markers approved for use in cosmetics or food have been tested by European Commission expert committees for toxicological safety, and the Pesticide Safety Directorate also view them as safe for manufacturers of pesticides to incorporate into their products, without the need for further safety tests.

Acid Blue 9 is an approved food dye. Published literature indicates it has a low acute oral toxicity rate of LD₅₀ > 2000 mg kg⁻¹ (Anon., 1999). The World Health Organisation would usually class a chemical with this level of toxicity as having a negligible hazard to users, providing routine safety precautions are taken (Willoughby *et al.*, 2004). However, contact with the concentrated dye might lead to slight skin or eye irritation (Albion Colours, 2005). No evidence of reproductive toxicity, carcinogenicity or mutagenicity has been found (Anon, 1999; Orme and Kegley, 2004).

Acid Blue 9 (as Dysol Turquoise) has a 24 hour LC₅₀ to rainbow trout of >300 mg l⁻¹ (Albion Colours, 2005; Orme and Kegley, 2004). For pesticide formulations, such toxicity ratings would usually attract a hazard rating of

‘not classified’ (i.e. not hazardous) (Willoughby *et al.*, 2004). In other words, there is good evidence to suggest that Acid Blue 9 is not hazardous to the aquatic environment. However, at high enough concentrations the dye can kill aquatic vegetation. Aquashade, a product containing 23.63% Acid Blue 9, plus 2.39% Acid Yellow 23, has been used in the USA as an aquatic herbicide, at a rate of 0.0006 g of product per litre of treated water (i.e. a 0.014%, or 140 ppm solution of Acid Blue 9 throughout the treated body of water).

Information on environmental fate is limited, but Acid Blue 9 is thought to photo- and bio-degrade within 8–16 weeks (MDAR, 2005).

There is only partial evidence of the effect of Acid Blue 9 on the wider environment. Nevertheless, given the lack of negative evidence, its low toxicity, and its approval as a food and cosmetic dye, it is reasonable to conclude that Acid Blue 9 is at least as safe for operators or the environment as any currently approved pesticide that it might be mixed with. It is already used in woodlands as a dye marker for urea applications (Spencer, 1998), and as a constituent of the biological control agent PG Suspension (active ingredient *Phelbiopsis gigantea*), both used to protect stumps from infection by the wood rotting fungus *Heterobasidion annosum*.

Table 1 summarises some of the toxicity characteristics associated with the food dye Acid Blue 9. For more details on how the above toxicological measures and pesticide hazard ratings are derived, how to select pesticides to lessen the risks of harm to operators and the environment, and for comparison with other additives and pesticides, see Willoughby *et al.* (2004).

Table 1

Summary of some published toxicity characteristics for Acid Blue 9 obtained from the world literature.

Colour Index name ¹	Colour Index number ¹	Rate applied (kg a.i. ha ⁻¹)	Rate applied (mg m ⁻²)	Toxicity to mammals (rats): oral (LD ₅₀ , mg kg ⁻¹) ²	Toxicity to mammals (rats): contact (LD ₅₀ , mg kg ⁻¹) ²	Toxicity to mammals (rats): NOEL (mg kg ⁻¹ by body weight) ³	Hazard classification ⁴	Hazard classification: aquatic toxicity (LC ₅₀ mg l ⁻¹) ⁴
Acid Blue 9	CI 42090	1.6	160	>2000	4600	>600	Food dye – not classified but effectively ‘Not Hazardous’.	>300 – not classified but effectively ‘Not Harmful.’

¹Colour Index Name and Number provide an internationally recognised system for identifying commercially available dyes (American Association of Textile Chemists and Colorists, 1999).

²Data obtained from the world literature, not generated by the Forestry Commission. LD₅₀ is a standard toxicological measure of the amount of chemical required to kill 50% of the test population, in mg of chemical per kg of bodyweight. For comparison, caffeine has an LD₅₀ of 192 mg kg⁻¹, sugar 29700 mg kg⁻¹, glyphosate > 5000 mg kg⁻¹ and cypermethrin 250–4150 mg kg⁻¹.

³NOEL is the rate, in mg of chemical per kg of bodyweight, that was found to have no observable effect when taken as part of the regular daily diet.

⁴Acid Blue 9 is a food dye, is not covered by pesticides legislation and so requires no pesticide hazard classification. However, pesticides with similar levels of toxicity would usually be classed as ‘not hazardous’ or ‘not harmful’.

Cost

Acid Blue 9 is commonly available from many industrial generic chemical suppliers as a relatively cheap, pure powder dye. It is also available in a pre-diluted form, such as the dye Dysol Turquoise ANX 50 Liquid (40% Acid Blue 9), which although more expensive, can be easier to handle. The cost of adding 1.6 kg a.i. ha⁻¹ Acid Blue 9 (as 4 l ha⁻¹ Dysol Turquoise) to dilute herbicide sprays is approximately £68 ha⁻¹ (Table 2). For post-plant insecticide sprays at 0.8% of final spray volume (as 2% Dysol Turquoise), the cost is approximately £10 ha⁻¹. Bulk discounts for dyes are available from many industrial chemical suppliers. Forestry Commission staff should consult the FC suppliers list for centrally negotiated contracts.

Using a dye marker may require rates of some foliar-acting herbicides to be increased up to the maximum rate recommended on the label to achieve good control of weed species that are difficult to kill. Hence the total amount of herbicide used in any one application may actually need to be increased, even though impact on non-target vegetation, the need for repeat treatment due to poor spray targeting, and the risk to operators from faulty protective equipment, would all be reduced. In addition, for some cheap foliar-acting herbicides such as glyphosate, in strictly financial terms it would prove more cost effective to make a repeat application to previously missed weeds, rather than try to improve initial targeting through using dye markers. Users will therefore need to balance whether the benefits of using a dye marker in any given circumstance outweighs its cost, and any risk they perceive from adding a further synthetic chemical into the environment. Willoughby *et al.* (2004) provide guidance on balancing the environmental risks associated with different forestry approved pesticides.

Table 2

Summary of the cost and application rates for Dysol Turquoise.

Common name ¹	Formulation	Approximate cost (£ litre ⁻¹) ²	Rate applied (litres ha ⁻¹) ³	Approximate cost (£ ha ⁻¹)	Rate applied, post-plant insecticide spray (% of final spray volume) ⁴	Approximate cost, post-plant insecticide spray (£ ha ⁻¹)	Supplier
Dysol Turquoise	40% Acid Blue 9	17	4	68	2	10	Albion Colours

¹Dysol Turquoise is listed here as one example of a pre-diluted dye (available from Albion Colours, www.albionchemicals.co.uk), but Acid Blue 9 is also commonly available from many other industrial generic chemical suppliers as a relatively cheap, pure powder dye.

²Indicative price only – bulk discounts for dyes are available from many industrial chemical suppliers. Forestry Commission staff should consult the FC suppliers list for centrally negotiated contracts.

³Recommendation is based upon an application rate of 1.6 kg a.i. ha⁻¹ Acid Blue 9 (i.e. 4 l ha⁻¹ Dysol Turquoise).

⁴Recommendation is based on an application rate of 0.8% Acid Blue 9 active ingredient in final spray volume (i.e. 2% Dysol Turquoise in final spray volume).

RECOMMENDATIONS

- Dye markers can help to reduce operator contamination, lessen the risk of crop damage through overdosing and drift, and help limit impact on non-target vegetation. Dye markers can therefore help reduce overall herbicide inputs through better targeting.
- Some herbicides are distinctively coloured and already show up adequately when sprayed, for example Stomp 400 SC (pendimethalin). These do not require the addition of a dye marker.
- If a pesticide product label recommends the use of a specific dye for a particular application type, follow this advice.
- When it might be advantageous to use a dye marker with a dilute herbicide spray, but no specific dye is recommended on the herbicide product label, then consider adding 4 l ha⁻¹ Dysol Turquoise, containing 40% Acid Blue 9 (or any other dye giving an equivalent of 1.6 kg a.i. ha⁻¹ Acid Blue 9) to the pesticide mix.
- Do not use Acid Blue 9 where glyphosate is applied at low rates on weeds that are difficult to kill.
- The visibility and persistence of dyes will depend on individual perception, the vegetation being treated, and on prevailing climatic conditions. A rate of 4 l ha⁻¹ Dysol Turquoise (or any other dye giving an equivalent of 1.6 kg a.i. ha⁻¹ Acid Blue 9) should be clearly visible when wet, and immediately after

spraying when dry, but subsequent visibility will vary. For this reason dye markers are of most value for the operators, and are unsuitable for follow up supervisory purposes unless higher rates are used (which may affect pesticide efficacy).

- For post-plant insecticide sprays, where a marker dye is required, use a 2% solution of Dysol Turquoise (to give an equivalent of 0.8% a.i. Acid Blue 9 in the final spray volume).
- The effect of adding dyes on pesticide efficacy has only been tested for permethrin, alpha-cypermethrin, glyphosate, asulam and propyzamide. Users must therefore carry out their own small-scale trials before engaging on large-scale treatment programmes using Acid Blue 9.
- Recommended rates for mixing with urea solutions, or for additional dyeing of PG Suspension in solution, are to use a 0.004–0.016% solution of Acid Blue 9 (equivalent to 0.04–0.16g l⁻¹), the lower rate being for harvesters where staining of timber produce during felling is at risk, the upper rates for high rainfall sites with infrequent supervisory visits. Higher rates of up to 0.065% Acid Blue 9 (0.65g l⁻¹) have also been successfully used in some instances to improve visibility where necessary. These rates of Acid Blue 9 can be achieved for example through using a 0.01–0.16% solution of Dysol Turquoise (equivalent to 0.1–1.6 ml l⁻¹).
- Acid Blue 9 is a food dye with low mammalian toxicity, and is unlikely to impact negatively on the environment.

- When assessing safety, treat any marker dye as another pesticide. Carry out a COSHH assessment, take the appropriate safety precautions, and add the dye to the tank mix at the same stage in the calibration process as other pesticides. All applications are made at users' own risk.
- If dye appears to be on the inside of protective clothing, this may indicate a fault in the equipment. Test by applying water to the outside of the clothing, with a paper towel held on the inside to show up any penetration of liquid. The presence of dye can also indicate poor hygiene practices, or inadequate levels of protective clothing.

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Useful websites

www.forestry.gov.uk/pesticides
www.forestresearch.gov.uk/vegman
www.mass.gov/agr

Disclaimer

The list of products in this Technical Note is not comprehensive; other manufacturers may be able to provide products with equivalent characteristics. Reference to a particular manufacturer or product does not imply endorsement or recommendation of that manufacturer or product by the Forestry Commission.

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