A FEW ALTERNATIVE TECHNIQUES FOR THE PRODUCTION OF OLIVE GREEN SHADE WITHOUT THE USE OF THE CONVENTIONAL SYNTHETIC DYESTUFFS

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ABSTRACT

Investigations were undertaken to explore the possibilities of dyeing cotton fabrics to olive green shade using only mineral pigments or other indigenous and cheap colouring matters. Materials dyed by using such compositions could be used for a variety of purposes, other than Service clothing, such as tentage, canvases, ducks etc. After studying the self shades obtained with various mineral pigments, several compatible combinations were tried out to get the correct olive green shade. It was observed that olive green shade with varying degrees of fastness characteristics can be produced by different compositions of mineral pigments with or without synthetic resin bindings. The choice of a specific recipe for dyeing a fabric will however depend upon the end-use of the fabric and the shade fastness characteristics expected of the same.

Introduction

Among the various Service shades, olive green has the widest application and a dyer is called upon to use his ingenuity in the production of this shade on a variety of textile fabrics with varying degrees of fastness characteristics. The most common methods for the production of this shade consist of the use of vat colours in conjunction with Minerial Khaki-Straight Vat combinations or sulphur colour combinations depending upon the shade fastness characteristics which are required of the fabrics in question. There have been occasions when there was acute shortage of appropriate vat or sulphur colours due to import restrictions. It was, therefore, considered worthwhile to investigate whether an olive green shade could be produced by alternative means which could avoid the use of the conventional synthetic dyestuffs.

There are three types of colouring matter applicable to textiles:

(*i*) Inorganic pigments which can be easily precipitated *in situ* in the fabric by double decomposition *e.g.*, hydroxides/oxides/carbonates of chromium, iron, copper, manganese, cobalt and nickel.

(*ii*) Inorganic pigments which cannot be precipitated in the fabric but are to be applied as such *e.g.*, ultra marine blue, lamp black etc. and

(*iii*) Pigments of organic origin *e.g.*, Aniline Black, Bhilawa Nut Black etc.

Hydroxides/oxides/carbonates of metals give quite fast shades but the range of colours is very limited. Ultra-marine and lamp black pigments possess little affinity for cotton and hence their application requires the use of fixing agents. Aniline black and Bhilawa black are developed on the fabric; the resultant shade which is rather dark is known to possess good all round fastness properties.

Experimental

In order to make a systematic study of the actual shade obtained by the use of inorganic chemicals, self shades in various concentrations of hydroxides/oxides/carbonates, and sulphides of Iron, Copper, Lead, Manganese, Chromium, Cadmium, Cobalt and Nickel were produced on cloth and their suitability and compatibility with each other for obtaining the OG shade was studied. Combinations of these shades were then examined. A reasonably accurate match to standard olive green was obtained by a combination of the sulphides of Iron, Chromium, and Copper but this shade lacked fastness to washing.

Attempts were then made to enrich the green component of mineral khaki which is a complex formed by the hydroxides/oxides of iron and chromium. This however did not give the desired depth of olive green shade. Prussian blue in conjunction with mineral khaki gave a deep shade possessing good light fastness but the colour leached out in alkaline media, such as soap. Resort was then taken to the use of ready-made pigments like Ultramarine, Monolites (ICI), Monastral (ICI) and Lamp black along with Iron and Chromium salts developed later into oxides. An approximate match was obtained on drill with Iron-Chromium-Lamp black combination. The shade was found to possess good fastness properties comparable with those of the conventional MK—Vat method but with the disadvantages of being costly and giving heavy loading to the fabric. Efforts to reduce the cost did not prove fruitful as only light depth of OG shade could be achieved by reducing the concentration of pigments.

Another recipe was evolved by using Aniline black in place of Lamp black along with Iron and Chromium oxides. This process gave a reasonably good match with the standard shade possessing excellent fastness properties. The process was however costly on account of the very high concentration of the chrome liquors required for loading the fabric to get the required depth of the olive green shade.

In order to evolve a recipe which would give the olive green shade at comparatively cheap rate and with low loading, experiments were conducted using Aniline Black and Lead Chromate (Chrome Yellow) both of which had high tinctorial value. Industrial scale dyeing based upon the above process was undertaken in a local mill. The study of the fastness properties of the shade dyed at the mill however revealed that it lacked in fastness to light due to vary pale shade of the Aniline black ground; otherwise the shade obtained by this process was cheaper and withstood the wash-fastness test (wash wheel test No. 4, four times) satisfactorily.

Efforts were then made to replace Aniline black by lamp black in the above process. Various synthetic/natural binders for fixing the pigments were tried *e.g.*, Badafin 2101 (ICI), Cashewnut shell liquid resin, Casein, Gelatin etc. A reasonably good shade with lamp black and Lead chromate fixed with Bedafin 2101 could also be produced.

The most promissing recipes which were found to produce an olive green shade are briefly described in the appendix to this paper. Their fastness characteristics, percentage loading and approximate cost of chemicals required in their production are also given along with similar details of a Trade sample which illustrates the quality currently being produced by the mills.

Discussion

Although a wide range of shades is available in mineral sulphides, they suffer the general drawback of hydrolysing during weathering. So to obtain the olive green shade, use can be made of Chromates for yellow orange shades. Iron Copper, and Manganese Oxides for buff/brown; Chromium, Nickel and Cobalt oxides/hydroxides for greens. Ferro ferricyanide (Prussian Blue) and ultramarines for blues, and different varieties of carbon for blacks.

Shades produced by Iron salts alone were found not to be suitable for ultimate production of olive green shade. Copper salts do not give reproducible results and, moreover, higher concentration of copper on the fabric accelerates actinic degradation and thus reduces the life of the material. Manganese salts alone were also found not suitable for dyeing the fabric into olive green shade. Shades produced by chrome yellow are sensitive to alkalies. They form the basic chromates ($PbCr0_4$ Pb0) and hence have to be after-treated with a mild alkali, like lime, to obtain a stable shade. Amongst the chromium salts *viz.* chrome alum, chromium sulphate and chromium acetate, only the last one yields deep and fast green shade. It, however, requires a high concentration of caustic soda (25%) for development. Theoretically a mixture of chrome green and manganese brown should give the desired olive green shade but owing to the incompatibility of the two pigments at the development stage the desired shade could not be produced; the optimum concentration of alkali for precipitation of chrome green being 25 per cent whereas that for manganese brown being only 10 per cent.

As a result of experimental trials, necessity was felt for incorporating a black pigment in the dyeing recipe as without it none of the combinations could give the depth of the standard olive green shade. Although inorganic black pigments like Ferroso Ferric Oxide (Fe_3 0_4) (obtainable by the oxidation of Ferrous hydroxide/carbonate), lead sub-oxide (Pb0), Cobalt oxide and Manganese dioxide etc. are known, it is impractical to produce them on the fabric. Silver salts give brownish black shade but they are rather costly.

Black pigments of organic origin *e.g.*, Bhilawa nut extract, in combination with mineral salts, gives a good black shade with satisfactory fastness to washing but the resultant shade, which is required only in a very low depth for the olive green formulation, is fugitive to light. Aniline Black which is known for its all round fastness properties in deep shade, also exhibits poor light fastness in lower depths. Lamp black is the only black pigment which possesses extremely good fastness properties but it has got little affinity for cotton. The use of binders, synthetic or natural is, therefore, necessary for fixing lamp black when used with other pigment.

Out of the various combinations of pigments tried, the following were the only ones which could produce a shade similar to the olive green and with reasonable degree of fastness.

(*i*) Iron Oxide—chromium Oxide—Lamp Black.

(*ii*) Lamp Black—Lead chromate fixed with Bedafin 2101 (a Urea—formaldehyde resin)

(*iii*) Lamp Black—Lead chromate fixed with cashewnut shell liquid resin.

(*iv*) Aniline Black—Iron oxide—chromioxide.

and (*v*) Aniline Black—Lead chromate.

The relative merits and demerits of each of these processes have been described at the appendix to this paper. Process No. (*i*) above has given a very good match to the standard olive green shade, its fastness properties are also comparable with those of the conventional M. K. vat supplies. However, the process is cumbersome, costly, and loads the material heavily. Processes No. (*ii*) and (*iii*) have also given good shades but fastness to washing has been found to be poor. Aniline-black ground shade topped with Iron and Chromium oxide gives a shade possessing all round fastness properties but also suffers from the drawback of heavily loading the facbric. Aniline-Black-lead chromate is a cheaper combination giving shade with good wash fastness properties but lacks in resistance to fading by light.

Conclusions

Alternative modes of manufacture of olive green shade without the use of the conventional synthetic dye stuffs can be employed for the production of olive green shade. Due to low tinctorial values of mineral pigments, however, it is not practicable to produce an olive green shade in the required depth of shade with the use of purely inorganic compositions. The depth of shade can be enhanced by the use of organic compositions such as Aniline Black, and inorganic pigments which have no affinity for cotton, can also be utilised along with suitable binding agents. The actual choice of formulation for dyeing a given fabric will however, depend on the shade fastness characteristics which are expected in the fabric.

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APPENDIX

Comparative merits of some of the combinations which produce the olive green shade on textile materials

Serial No	Process	Fastness to light	Fastness to Washing as per wash wheel test No			Fastness to Leaching (under Bundesman)	Cost of Chemicals per yard	Loading per cent	Remarks
			2	3	4				
1	2	3	4			5	6	7	8
1	All mineral pigment process Chromium Acetate—45% Iron Sulphate—1% Lamp Black—0·5% Monastral Green GS—0·2% Develop in 25% Caustic Soda Solution.	Above Class V	Good	Good	Good	Stands 96″ equivalent of rainfall.	Rs. 0 8 0	32·5 %	Good solid shade, possessing excellant light and washing fastness but process is cumbersome.
2	Lamp Black—Lead Chromate (fixed with Bedafin 2101) (*a*) Chrome yellow—3·2% (*b*) Topping in: Lamp Black—1·6% Bedafin 2101—5%	Do	Good	Good	Poor	Do	0 3 5	8%	Good shade. Stands wash wheel test No 2 and 3 but under test 4 much of the yellow component is lost. Light fastness is good.
3	Lamp Black—Lead Chromate (fixed with Cashewnut shell liquid resin) (*a*) Chrome yellow—3% (*b*) Topping in: Lamp Black—0·9% Monastral fast—0·7% Blue BS C.N.S.L. resin—10%	Class IV	Good	Fair	Poor	Do	0 2 6	6%	Good shade. This process could be used where a high wash and light fastness is not essential.

4	Aniline Black—Iron Oxide—Chromium Oxide (*a*) Aniline Black—0·5% (*b*) Topping in: Chrome acetate—40% Iron Sulphate—3% Development in 25% Cuastic Soda Solution	Class V	Good	Good	Good	Do	0 7 0	20%	Shade slightly lighter than the standard. Light and washing fastness satisfactory.
5	Aniline Black—Lead Chromate (*a*) Aniline Black (single bath)—3% (*b*) Topping with— Chrome yellow—3%	Class III	Good	Good	Poor	Poor Does not stand 48" equivalent of rainfall.	0 2 8	6·5%	Good shade. On washing, tone changes to grey. Light fastness poor.
6	Mineral Khaki Topped Vat	Above Class V	Good	Good	Good	Excellent	0 5 8	App. 8%	