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ROMANIA

Technical report: Manufacture of ceramic decals

Prepared for the Government of Romania by the
United Nations Industrial Development Organization,
executing agency for the United Nations Development Programme

Based on the work of Ray Andrews, ceramic colour expert

United Nations Industrial Development Organization
Vienna

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SUMMARY

Ball mill grinding of ceramic colours was improved resulting in an 80% reduction in grinding time, improved particle size distribution and improved gloss of colour surface.

Colour testing and matching was improved by introducing a new technique.

Good glass decals were made for the first time and overglaze decals were made by using both a printing vehicle and a covercoat based on a solution of normal butyl methacrylate.

Progress was made in the development of underglaze decals.

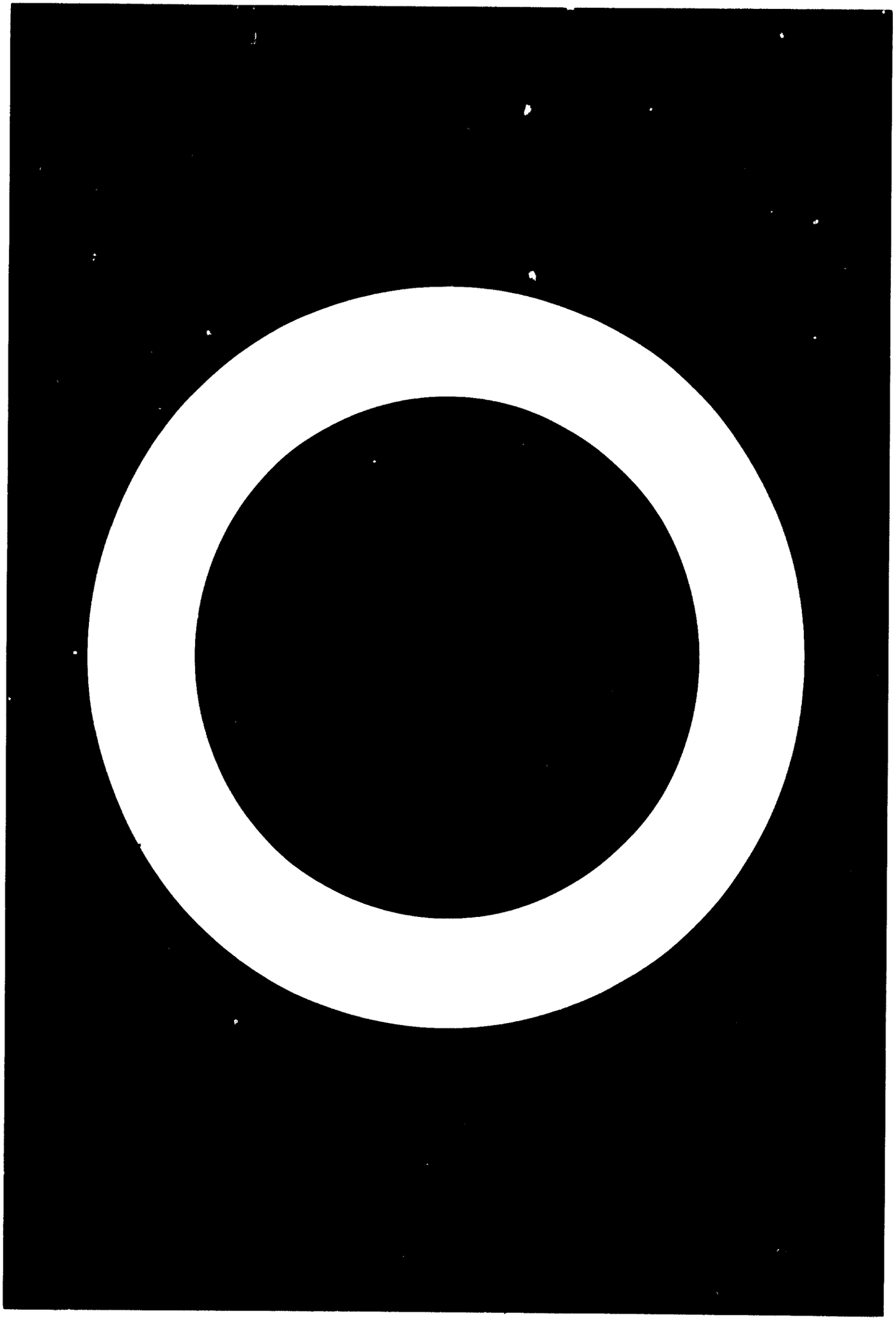
A programme was recommended to improve the Romanian decal paper.

Silk screens were improved by stretching the nylon while wet. Additional improvement will be made when polyester silk is used to replace nylon and the present screen emulsion is replaced with Azcool.

Used screens, which were no longer needed, were recovered by soaking in a solution of Sodium Hypochlorite and scrubbed with a stiff nylon brush.

A study of offset printing (lithography) is recommended.

To give insight into the materials used in ceramic colours, printing vehicles and covercoats, a list of representative materials is given.



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INTRODUCTION

The purpose of this mission was to give assistance to the people at the Institute for Glass and Fine Ceramics in Cluj-Napoca, in the manufacture of ceramic decals made by the silk screen process of printing. After a short stay it was learned that two months was not enough time to accomplish the necessary work, so the mission was extended for an additional month. It was also quickly learned that many of the problems originated in the colour manufacturing. While not included in the original plan the area of study was expanded to include ceramic colour manufacture as well as improvements in ceramic decals.

FINDINGS

Grinding

Grinding ceramic colour was a considerable problem. Grinding time was excessive (up to 96 hours per charge) and particle size distribution was poor. After grinding, the colour contained a high percentage of extremely fine material and some particles larger than desirable. The grinding balls used were a mixture of three sizes, 2 cm, 3 cm, and 5 cm.

Test grinds were made using only the 2 cm balls. In a 4 liter mill the ball charge was increased from 2 kgs to 6 kgs and the colour charge was 1,250 gms. The frit for the mill was screened through a screen having 7mm openings. This eliminated large pieces which will not grind.

This procedure reduced grinding time from 96 hours to 14 hours. Particle size distribution was improved and the colour fired with a better gloss.

In most cases colour charge was correct, but an insufficient ball charge was used. The ball charge was light enough that the grinding balls were completely submerged in the colour slurry. With this procedure the balls tend to float in the high density colour slurry and do not create sufficient friction for good grinding.

A good rule to follow for ball mill grinding is to use a sufficient weight of balls that they will extend at least 2 cm above the colour slurry. The total mill charge should occupy about 70% of the mill volume.

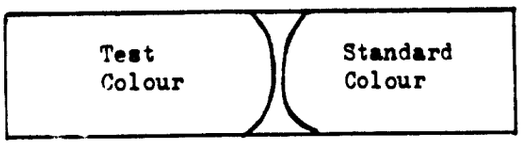
A design for a set of rolls was developed. These will be built at a later date. With these rolls it will be possible to pass the molten fritt through them as it comes from the melting furnace. This will form a ribbon about 2 mm thick which will go into water and break up into a size which will grind well and will not require screening.

Colour Testing

When developing new frits and pigments it was the practice to make a colour up in a printing vehicle, print decals, transfer and fire them. This procedure often required as much as five days.

It was demonstrated that colour can be rapidly and accurately tested by making a finger rub. In this procedure, the colour to be tested is rubbed up in water, or a mixture of water and denatured alchohol, using a flat glass plate and steel spatula for mixing. This colour slurry is applied to a small piece of single strength window glass by picking it up with the middle finger and making a smear on the glass. In the case of overglaze colour, it is applied to a small piece of glazed china or semi-vitreous ware. The test piece is then placed in a small laboratory furnace, which has been preheated to the proper temperature and allowed to remain there for 15 minutes. It is then removed and allowed to cool.

When matching colour or testing established colour it is the usual procedure to make the test on a piece of single strength window glass about 2 cm wide and 7 cm long. The standard colour is rubbed on the right hand side of the glass and the test colour on the left. Each colour is marked for identification. The following sketch illustrates the procedure.



These tests were fired in a small laboratory Glo-bar furnace, which is not suitable for this type testing because of the large amount of radiated heat from the top of the furnace. It was suggested that at least 2 laboratory furnaces containing nickle-chrome wire heating elements be obtained.

Screen Decals

At the present time the only decals produced are overglaze for china and semi-vitreous ware.

Part of these are printed on thermoflat paper obtained from England and the balance on a domestic Romanian paper.

The printing presses are the flat bed type and are loaded and unloaded by hand.

Printing Oil

The printing vehicle used presently is obtained from Siegle in Germany. It appears to be a plasticized solution of ethyl cellulose. This vehicle, used with a covercoat of butyle methacrylate produced a decal which is prone to fire with numerous small holes and cracks, and it is impossible to produce a suitable decal for application to glass with it.

The overcoat used is obtained as a 50% solution of normal butyl methacrylate dissolved in a fraction of petroleum solvent rich in xylene.

Since it is well known that butyl methacrylate will produce an excellent printing vehicle, this solution was tested as a printing vehicle for glass colours, overglaze colours and underglaze colours. It was found to work very well in each case except it dried very much too fast.

This butyl methacrylate solution is known in Romania by the trade name of Crilorom.

Since normal butyl methacrylate in pure resin form is not available in Romania, the resin was obtained by distilling off the solvent from the Crilorom and replacing it with an aromatic petroleum solvent having an initial boiling temperature of 200°C. This solution was further diluted with the petroleum solvent to produce a printing vehicle containing 40% normal butyl methacrylate.

This worked very well as a printing vehicle for glass decals, overglaze decals and underglaze decals.

The covercoat used was the Crilorom solution diluted with mineral spirit.

Covercoat

After the colours are printed on a decal, a clear lacquer is screen printed over the coloured impression. The purpose of this is to give the decal strength for the transfer operation and to hold printed matter such as letters or digits in position. Normal butyl methacrylate produced a very good covercoat except it is soft and when decal sheets are stacked they will block, that is they will stick together. To prevent blocking, a slip sheet is placed between each sheet of decal. This prodedure is expensive and time consuming.

It was demonstrated that 5% addition of cornstarch could be added to the covercoat and this will harden it sufficiently that blocking will not occur and the slip sheet can be eliminated.

Glass Decals

Decals for application to glass have never been made in Romania. Many tests have been made using Siegle Oil as a printing vehicle. and the Crilorem solution as a coverocat. All of these were unsuccessful due to the decals firing with numerous small holes and cracks.

Very good glass decals were made by using the printing vehicle described under the subject Printing Oil and covercoat of Crilorom solution.

Underglaze Decals

It is the opinion that at the Institute in Cluj that under glaze decals would be highly desirable because of their excellent protection from chemical attack, from such materials as fruit acids, vinegar and dish washing detergents.

The decals would be applied to the ware after it comes from the bisque kiln. This fire would burn away the organic material in the decal and attach the colour to the body. The ware is then fired through the glost kiln.

To use underglaze decals, the ware mush be fresh from the bisque kiln. Ware from storage has absorbed water from the atmosphere and will cause numerous small holes to appear in the decal when fired.

Because bisque ware absorbs water very strongly it must be sized before the decals are applied. A plasticized solution of ethyl cellulose, normal butyl methacrylate or poly vinyl alchohol will do very well. The size is dried and the decal applied.

Pigment mixed with 50% of soft fritt was found to work very well as underglaze colour.

Decal Paper

Some decal paper is obtained from Brittains Ltd., Stoke-on-Trent, England and part is of Romanian manufacture. The English paper works very well. However, problems are experienced with the domestic paper.

The Romanian paper will not remain flat, but curls very badly. It causes the colour to blister and fire with numerous small holes and cracks.

To make the paper, a barrier coat of starch is applied to one side. The paper is then given a coating of dextrin containing a small percentage of gelatine. A second coating of dextrin is applied which contains about 7½% glycerine. Both geltain and glycerine are very difficult to burn away and glycerin absorbs atmospheric water.

It was recommended that the gelatine and glycerine be replaced with polyethlene glycol no 400 or no.600. The following tests for a paper coating were suggested to prevent water absorption from the atmosphere.

Dextrin		90	80	70	95	90	85
Poly Etylene Glycol	400	10	20	30			
Klucel					5	10	15

Klucel is Hydroxy Propyl Cellulose and is available from Hwrcules, Inc., Wilmington,Delaware, U.S.A.

All the decal paper is very roughly handled so the size on the paper is damaged and edges of the paper are broken. It was shown how the paper should be handled and a strong recommendation was made that this improved technique be followed.

Printing Press Room

The press room was found to be very dusty, also the temperature and humidity in the room were not controlled. Each small particle of dust on a decal causes it to fire with a defect in the colour.

Both temperature and humidity affect the dimensions of paper so if these change during printing it is impossible to have good registration of colours.

It was recommended that the temperature of the press room be held between 65°F and 70°F and the relative humidity be kept at about 65%.

Silk Screens

Screens are presently made of nylon. Especially in cold weather the rubber squeegee passing over the screen generates static electricity. This causes the decal paper to adhere to the bottom of the screen and delays production. It also causes printing defects. Because of the stretch characteristics of nylon it is difficult to stretch properly.

A sample of polyester silk was obtained from the United States and tested. This gave good results, as polyester does not create the problem of static and stretches quite well.

A sample of an improved screen was no longer needed, the nylon was removed from the screen frame and destroyed. Especially proof screens which are usually used for only a very few prints, were being destroyed while they were still in new condition

It was demonstrated that screens can be recovered and reused by soaking them for about 20 minutes in a 1% solution, or stronger, of sodium hypochlorite. The screen is then placed in water and brushed with stiff nylon brush. After rinsing with water it is ready for reuse.

Good silk bolting cloth, used for making silk screens, is only available from Switzerland. It is very expensive and represents foreign exchange. It is, therefore, important to obtain maximum tension in the silk.

Offset Printing

A small offset printing press should be obtained and a development programme undertaken to produce this type decal.

Most overglaze decals for the decoration of china and semi-vitreous ware are printed by this process.

Colour for offset printing usually contains more pigment than is used in colours for screen printing. After grinding, the dried colour is mixed with a water solution containing casien and poly ethylene glycol 4000. About 2% each of casien and poly ethylene glycol 4000, based on the dry colour weight are used. After mixing the colour is dried, pulverized and is ready for use.

The vehicle is bodied linseed oil to which has been added a dryer. This very heavy oil is printed on to the paper and the colour, prepared as described above, is dusted into the tacky impression. Each colour requires a pass through the press and dusting operation.

When the design is complete a covercoat is applied by silk screen.

This cover coat is usually a solution of ethyl cellulose modified by an addition of a suitable plasticizer.

Some useful formulations were suggested, see Annex I.

FUTURE WORK

If the ceramic colour industry and ceramic decorating are to be brought to maturity in Romania, a programme should be undertaken to develop colours and vehicles for direct application to glass and to a lesser extent to china and semi-vitreous ware.

An effort should be made to develop at least two hot colour vehicles. One for first colour application and one for second colour application. These vehicles are thermoplastic and are solid at room temperature but liquid at temperatures of 150°F and higher.

They are used throughout the world for the high speed, multiple colour printing of such items as beverage bottles, drinking glasses and cosmetic containers.

One or more squeegee oils should be developed. These are liquid at room temperature and serve as the printing vehicle for ceramic colour.

Work should be undertaken to improve fritts for glass and overglaze colours. There is a need for better acid,alkali and detergent resistance. See Annex II.

The line of ceramic pigments could be improved and expanded. See Annex III.

RECOMMENDATIONS

1. Frit should be screened through a screen with 7 mm openings before charging into the ball mills.
2. Grinding balls should be one size, about 2 cm to 3 cm.
3. Total mill charge should (balls plus colour) fill 70% to 75% of the mill.
4. Sufficient grinding balls will extend at least 2 cm above the colour slurry in the mill.
5. A design for a set of rolls was suggested which will produce a ribbon of fritt suitable for grinding.

6. Finger rubs are suggested as a fast means of testing and matching colour.

7. A solution of normal butyl methacrylate should be obtained which is in an aromatic petroleum solvent with a boiling range of 200°C to 220°C and a K. B. value of at least 90.

8. A programme to improve the Romanian decal paper is outlined.

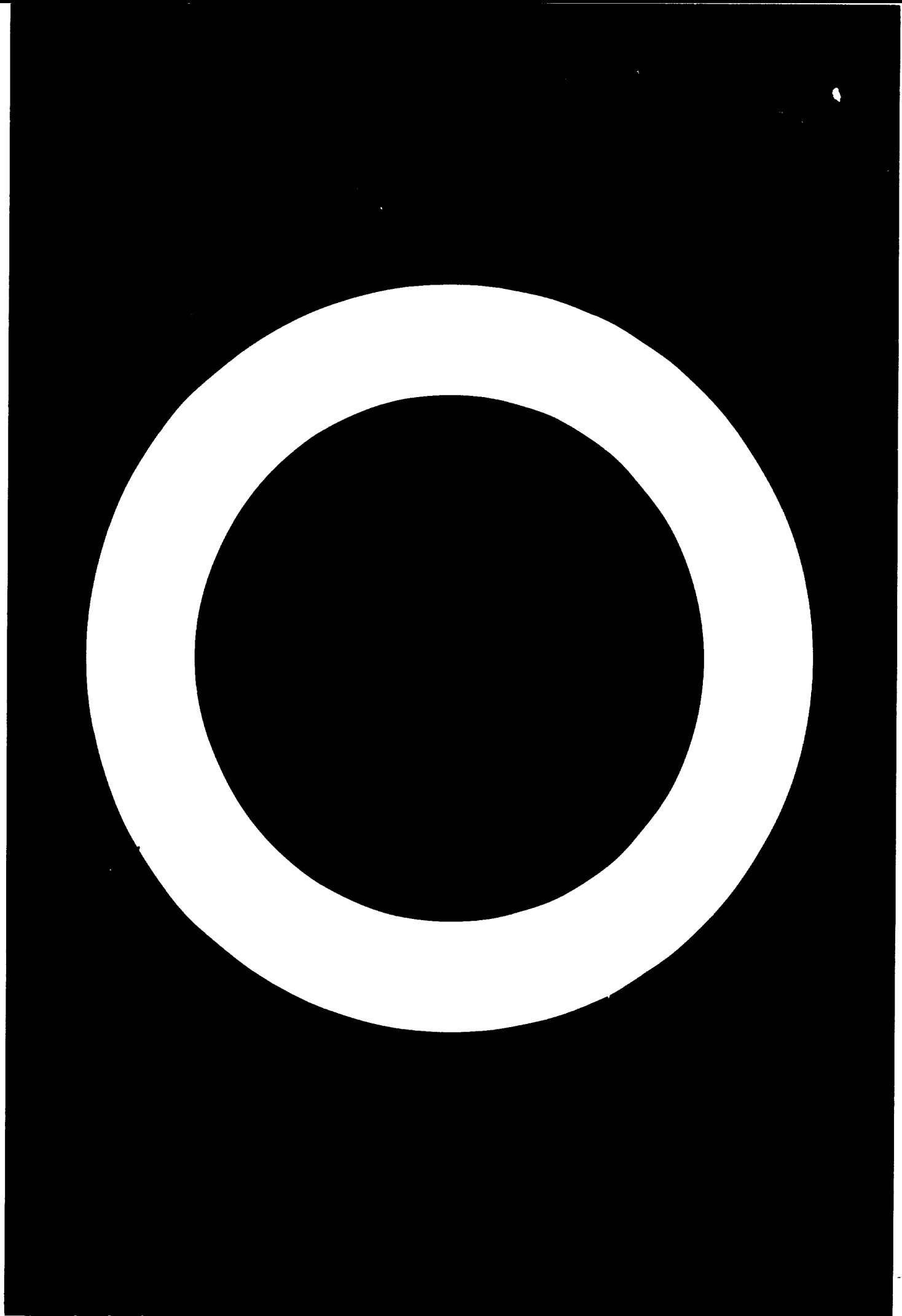
9. The printing press room should be clean and free of dust, with the temperature controlled between 65°F and 70°F and a relative humidity of about 65%.

10. When the screen fabric is nylon it should be stretched wet.

11. Screens no longer needed can be reclaimed by washing in a solution of sodium hypochlorite.

12. A programme for future work is recommended which would include the development of improved frits, a larger colour palette, thermoplastic printing vehicles, a squeegee oil and a study of lithographic printing.

13. A list of much needed equipment intended for consideration by UNIDO is listed in Annex IV.



Annex I

USEFUL FORMULATIONS FOR OFFSET PRINTING

DECAL COVERCOAT

Solvesso 100	40
Cellosolve	40
EthylCellulose N-22	18
SAIB	18

PRINTING VEHICLE

Solvesso 150	30
Butyl Cellosolve	30
Elvacite 2044	40
Lecithin	1

PRINTING VEHICLE AND COVERCOAT

Solvesso 150	30
Butyl Cellosolve	30
Elvacite 2044	30
SAIB	10
Lecithin	1

Solvesso 100 and 150 - Are high boiling aromatic petroleum solvents by the Standard Oil Company.

Cellosolve - ie ethyleneglycol mone ethyl ether

Butyl Cellosolve - ie ethylene glycol - butyl ether. Both are produced by Dow Chemical Co. and Union Carbide.

Elvacite 2044 - is normal butyl methacrylate. It is produced by E.I. Dupont.

SAIB - is sucrose acetate isobutyrate. It is produced by Eastman Chemical Co., Kingsport, Tenn., U. S. A.

Lecithin - is a heavy dark coloured oil produced from soya beans. It is used very extensively as an emulsifying agent in chocolate candy and various food stuffs. It is usually available in health food stores.

Annex II

USEFUL FRIT FORMULAS

Extra Soft Frit - Melting Temperature 850°F.

Pb_3O_4	330
H_3BO_3	75
SiO_2	30

Soft Flux - Melting Temperature 950°F.

Pb_3O4	300
SiO_2	45
B_2O_3	39

Soft Flux - Melting Temperature 1100°F.

PbO	200
B_2O_3	34
$Si\ O_2$	76
AlOh	6
CdO	6

Beverage Bottle Flux for White Enamel

PbO	59.4
SiO_2	29.5
$Na_2B_4O_7$	4.0
$Zr\ Si\ O_4$	4.0
NaF	2.4
Na_2CO_3	1.0
Na_2SO_4	0.25

Annex III

PIGMENT FORMULAS

Brown Pigment

ZnO	490
Fe_3O_4	340
Cr_2O_3	430

Dry mix and pulverize. Caloine at 2400°F.

Blue Green Pigment

ZnO	131
$MgCo_3$	787
Co_3O_4	548
Cr_2O_3	2407
Al OH	316

Dry mix and pulverize. Caloine at 2350° F.

Black Pigment

Fe_3O_4	389
Co_3O_4	325
Cr_2O_3	291

Dry mix and pulverize. Caloine at 1950°F.

Yellow Pigment

Sb_2O_3	240
Ti O_2	240
Pb $_3O_4$	840

Dry mix and pulverize. Caloine at 2000°F.

Annex IV

RECOMMENDED NEW EQUIPMENT

The following equipment would be very useful.

1 or 2 - Electric Laboratory Furnaces
Muffle opening 10 cm X 14 cm X30 cm (approx.)
Nickle-chrome heating elements
Chromel-Alumel Thermocouple with out a protection tube.

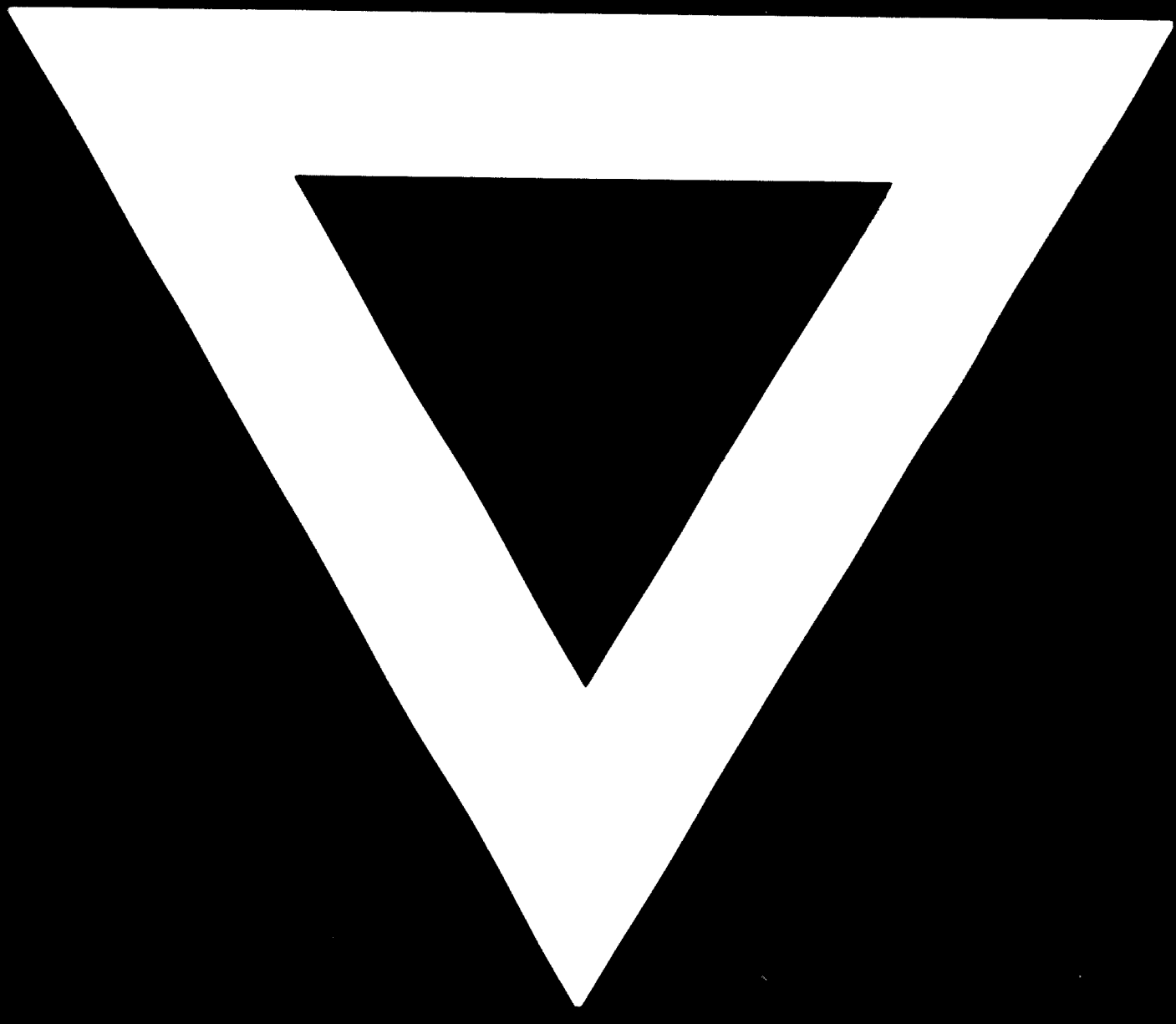
The above should have a combination pyrometer and controller.
Cost: Approximately $ 1200.00 each.

1 - Small Laboratory 3 rool paint mill.
The robls could be as large as 7 cm diameter and 20 cm long.
The rolls should be water colled
Cost: Approximately $ 3500.00

1 - Production Size Wicket Dryer
This would be used to force dry the decals after printing.
Decals are now air dried at room temperature. This allows dust to gather on them. Every speck of dust on a decal causes a hole or other defect in the fired decal.
Cost: Not Known

1 - Small Offset Printing Press
Cost: Not Known

C-700



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