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ENAMELS:

THEIR MANUFACTURE AND APPLICATION TO IRON AND STEEL WARE.

BY

LAURENCE R. MERNAGH,

B.Sc., F.I.C., A.C.G.F.C., F.C.S.

With 19 Illustrations and Folding Tables.

LONDON:
CHARLES GRIFFIN AND COMPANY, LIMITED,
42 DRURY LANE, W.C. 2.
1928.

Printed in Great Britain
by Bell & Bain, Limited, Glasgow.

PREFACE.

THIS work is addressed to all engaged, or otherwise interested, in the production of enamelled iron and steel ware for commercial and industrial purposes—that is to say, in true vitreous enamelling involving the use of high temperatures; it is in no way concerned with stoving, cold processes, the enamelling of non-ferrous metals, or general decorative work.

It is intended to include both cast iron and steel enamelling and the two sub-divisions of the latter, hollowware and flat work, and where examples are required, hollowware has been almost invariably selected. The majority of the remarks, however, apply equally well to all branches, any exceptions being noted, and some remarks on cast iron being collected together in Chapter XI.

The most ardent optimist would scarcely consider the story of enamelling to be the brightest page in Britain's industrial history, for, in spite of the natural advantages in coal and iron we enjoy, various other conditions have acted against our occupying a pre-eminent position. Originating in Germany, the industry has expanded and developed there, in other continental countries, in America, and in this country. Though practised for many years before, enamelling only achieved important proportions here during the Great War, and then prospered until exposed to the full blast of the well-matured continental competition. Despite the hopes and promises aired in the post-war days regarding the protection of new industries against this unfair competition, the Government has within the last two years seen fit to decline the application for protection from the hollowware manufacturers, though at the time of going to press, the re-opening of the subject is considered imminent.*

Enamelling is an intricate process and exceptional in its dependence to a very great extent upon high quality manual labour. Either the industry in this country has not been practised long enough to have trained a sufficiency of specialised labour, or the industry is not wealthy enough to pay the wages necessary to attract the right type.

The industry suffers to a certain extent by internal and external competition. Steel hollowware has adversely affected the cast-iron enameller, though the latter is now enjoying a good innings with household baths and stove parts. The public fancy for increased press advertising has not improved the business of the sign plate maker, who may be further affected by the intention of prohibiting enamelled signs on buses and trams. As a compensation, however, enamelled kitchen cupboards, table tops, and stove parts are demanding more enamelled sheet steel.

German and American writers readily acknowledge their progress in enamelling to be due to the application of science to their industry. J. B. Shaw, introducing his treatise mentioned below, writes :—

" Within the last twenty years, the ceramic industries of the U.S.A. have made great improvements in the quality of their products due to the abandonment of rule of thumb methods which marked the beginning of the industry, and the application of scientific principles in manufacturing processes."

In this country one or two manufacturers have flirted with science to the extent of employing trained men, and then usually ensured that the bulk of their time should be devoted to non-technical work, whilst any remaining for experimenting should be given to a dictated policy, usually the impossible idea of a lay mind. One or two more occasionally invite the aid of an analyst when things go wrong, and useful though these small investigations are, the fundamental problems of the industry such as the abolition of the coloured ground coat, the finding of a satisfactory substitute for tin oxide, and the action of salts on clay suspensions will never be satisfactorily concluded by a piece-meal worker attending to a dozen other matters either inside or outside the factory.

The industry in this country is in the hands of the so-called practical man, an indispensable asset to any manufacture, but it is respectfully suggested that for real progress to be made, and to strengthen his own position, he must reduce both his contempt for his brother enameller, and his fine scorn for scientific methods. Trade secrets die hard, and these will always be retained to a greater or less extent, but surely the time is ripe for a little less secrecy and jealousy among enamellers and a little more pooling of knowledge with open discussion of fundamentals. The enameller gladly accepts new and improved colours from the colour maker, and improved steels, all the direct result of chemical investigation, yet generally denies his ability to help in the more immediate problems of enamelling. Recent happenings indicate that the time is approaching when enamellers must either hang together, or else hang singly, and unfortunately there are some who would prefer to expire in the noose of foreign competition than ask their neighbour to help them out of it.

If the Government failed the industry when protection was desired, it had previously offered a helping hand through the Department of Scientific and Industrial Research. On certain conditions this department will advance to an industry (not an individual firm) half the money required for financing a research and experimental station with a full-time staff. Most of the wealthier industries have availed themselves of the opportunity and are loud in their praise for the results achieved. Though it is too much to hope for the immediate installation of an enamel research station, it may become a reality in the days to come.

One method of stimulating thought and directing attention to the essentials of the industry is by means of literature, and in this we are sadly lacking, a state of affairs recently deplored by the manager of one of our largest works. Apart from brief notices of experimental work in the purely scientific journals, a trade monthly, *Ramsden's Bulletin*, appears to be the sole representative of journalism devoted entirely to English enamelling. There are, of course, the translations of the late Dr. Grünwald's three excellent books, " Raw Materials of the Enamel Industry," " The Theory and Practice of Enamelling on Iron and Steel," and "The Technology of Iron Enamelling and Tinning" (all published by Messrs. Griffin), and also an earlier translation of a German work. The American Government, since the war, has published three useful works, entitled :—

"Enamels for Sheet Iron and Steel," J. B. Shaw ;

"Materials and Methods used in the Manufacture of Cast Iron Wares," H. F. Staley ;

"Wet Process Enamels for Cast Iron," Danielson and Reinecker ;

for all of which the writer expresses his appreciation, and for the first two in particular his great indebtedness.

In a class by itself is the *Journal of the American Ceramic Society*, which monthly publishes original work connected with enamelling, and is indispensable to the serious student of the subject. Papers which have appeared here are frequently abstracted in the monthly journal, *Ceramic Industry*, which is an excellent publication, and the same remark applies with only slightly less force to *The Enamelist* and *The Ceramist*, all three of American origin. Turning to the German publications, more caution is necessary, as there is an abundance of literature, some good, and some indifferent, and in addition to a good knowledge of German, some acquaintance with the status of the writer is advisable, and an ability to sort the chaff from the wheat. The various journals catering for enamellers include :—

Emaillierwaren Industrie (weekly).

Illustrierte Zeitung fur Blechindustrie (weekly).

Keramische Rundschau (weekly).

Emailletechnische Monats Blätte (monthly).

An excellent handbook is Vielhaber's "Rezeptaschenbuch."

In addition to thanking Messrs. Avery, Ltd., Messrs. British Insulated Cables, Ltd., and C. Hasle, Esq., of the firm of A. Hermansen, for blocks and permission to reproduce, the writer's best acknowledgments are due to many friends too numerous to mention for assistance gladly given in the compilation of this work.

He cannot close, however, without expressing his special gratitude to Mr. W. Regan, B.Sc., A.R.T.C., etc. (Head of the Chemical and Metallurgical Dept. of the Wolverhampton and Staffordshire Technical College), and to Mr. J. B. Brockbank, B.Sc. (of Messrs. Bostock & Hargrove, Consulting Engineers, Wolverhampton), without whose help the sections on steel and cast iron, together with the photographs, could not have appeared.

L. R. MERNAGH.

WOLVERHAMPTON, *June*, 1928.

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* Just as this work goes into print, the official announcement arrives that a duty of 25 per cent. is to be imposed upon imported enamelled hollowware. This, coming as an extremely pleasant surprise to the home manufacturer, should prove to be the salvation of the industry, and the starting-out along a new road of scientific progress.

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ENAMELS:

THEIR MANUFACTURE AND APPLICATION TO IRON AND STEEL WARE.

CHAPTER I.

THE STEEL BLANK.

THE material most largely employed for the manufacture of enamelled ware is best South Wales blackplate—that is, a steel made by the Bessemer, or open hearth process, and which appears on the market in a quality known as "pickled and close annealed." The chief requirements for hollowware are capacity for deep drawing, and high tenacity. These have led to the adoption of a newer material, Armco iron, a pure iron, which has consequently good drawing qualities and is absolutely regular in action. Owing to extra trouble and longer duration of manufacture, this material is more expensive than mild steel, and is consequently prohibitive where cheaper quality ware is being manufactured for a highly competitive market, but the material gives an excellent result, and is gaining popularity for sign plate manufacture.

The Siemens open hearth process depends on the heating of pig iron and scrap in a gas-fired regenerative furnace, hæmatite ore (ferric oxide ore) being added after the charge is molten to oxidise out the impurities. The charge may be up to 100 tons, and purification is continued until the right amount of carbon remains in the metal, when it is tapped out, a small quantity of ferromanganese being added as the steel runs into the ladle. Two types of material are available for lining the hearth of the furnace, one acidic and the other basic. The former is composed of silica, and if used, only the carbon, silicon, and manganese content of the pig iron become reduced during the process, the sulphur and phosphorus remaining unchanged, whilst in the case of a basic hearth consisting of dolomite, the proportion of sulphur and phosphorus is also lowered.

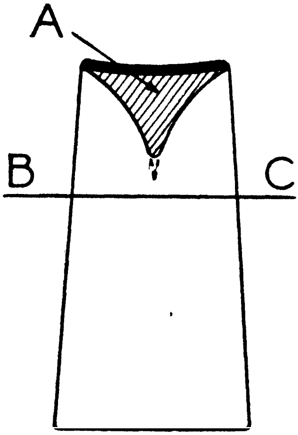

Fig. 1.—Cross-Section of Steel Ingot.

The molten metal from the furnace is tapped out into a ladle and is then run into moulds to form ingots, a cross-section of one being shown in Fig. 1. The shrinkage on cooling causes the core formation indicated, and as the impurities lower the solidifying point of the metal, these are to be found in the portion which solidifies last—that is, Section A. The ingot should be cut at the line B C, about one-third of its height down, the upper portion being rejected. If material from above B C is included, slag is introduced into the steel, causing trouble in any subsequent stamping operations, and during the enamelling process.

Divers opinions exist as to the ideal composition of an enamelling steel, many having their origin in prejudice. The successful enamelling of steels of very variable composition has led the author to the conclusion that within certain comparatively broad limits the chemical composition is of secondary importance to its physical condition. The evidence of the successful enamelling of both pure iron, and cast iron containing large and varying amounts of carbon, silicon, manganese, and phosphorus, cannot be ignored, and the rough and ready rule may be applied by the hollowware enameller that if the metal will satisfactorily withstand the drawing and other mechanical treatment to which it is subjected it is suitable for enamelling. Steels for our purpose require no peculiar treatment, the usual process of alternate heating and rolling until the required gauge is attained, meeting the case. The sheets are then cut to size, pickled in hot sulphuric acid, and annealed in an enclosed furnace for some hours, after which the material should be suitable for deep stamping operations.

The gauges of metal required range from 16 to 30, their thickness and weights being shown in the attached table.

TABLE I.

Gauge.	Thickness in Inches.	Thickness in Millimetres.	Wt. in Lbs. Per Sq. Ft. (Iron).
16	0·0625	1·590	2·50
18	0·050	1·270	2·00
20	0·0375	0·954	1·50
22	0·03125	0·794	1·25
24	0·0250	0·635	1·00
26	0·01875	0·476	0·75
27	0·0171875	0·437	0·6875
28	0·015625	0·397	0·625
29	0·0140625	0·357	0·5625
30	0·01250	0·317	0·50

The enameller requires a steel low in sulphur and phosphorus, and free from gas pockets and slag inclusions, and as the presence of these would render the metal unsuitable for most of its projected uses, he has the protection of the popular requirement behind him. The following table shows the generally accepted maximum percentage of materials other than iron, the second column showing Armco iron for comparison purposes :—

TABLE II.

Element.	Steel.	Armco Iron.	A Typical Analysis of Enamelling Steel.
Carbon, . .	0·20	0·02	0·11
Sulphur, . .	0·05	0·01	0·043
Phosphorus, . .	0·04	0·008	0·036
Silicon, . . .	0·02	Nil	0·010
Manganese, . .	0·40	0·06	0·065

The material arrives at the factory either in long sheets or more usually for the hollowware manufacturers in trimmed squares that may be used with minimum wastage. These vary in size from a few inches square upward, by half inches or quarters in either direction. Most hollowware requires to be drawn by dies in a power press, and spun with formers in a lathe ; other work is stamped into shape and the two edges joined by methods to be discussed later. The first operation is circling—that is, cutting the largest possible circle from the square supplied, either by means of a blanking press, or by a shearing machine. The waste corners are used for small articles if of sufficient dimensions, otherwise they are bundled together and sold as scrap. A deep article requires to have three or four draws, the machine employed being a toggle press. The dies are constructed of hard quality, close-grained cast iron. They are expensive and valuable implements, but useful only for the one particular design. The newer presses are multi-action, which as the name implies, do more than one draw in an action. For deep stamping purposes a highly ductile material with high tensile strength is required, hence phosphorus and sulphur must be reduced to a minimum. Virtually the only faults caused by defective composition are due to gas and slag inclusions, the former often showing up in the form of big blisters during pickling or subsequent heating, the latter as regular streaks, of small blisters. Their regularity and presence on both sides of the sheet may usually be regarded as complete evidence of faulty steel, and other causes should be sought for defects not conforming to these conditions.

During drawing operations it is usual to anneal after every second or third draw, this process of annealing being the heating of the shell to 750°–800° C. in a muffle, semi-muffle, or open furnace. The fuel may be coal, oil or gas, according to size and facilities available ; the duration of heating is about three minutes, and, to achieve the object, slow cooling is essential. Where this is not done a hard surface is obtained, useless for further drawing. Where drawing is followed by spinning, it is usual to anneal at least after the second and fourth draws. Deep drawing has been partly superseded by stamping two or more parts and then joining them ; for example, the body of a tall kettle is no longer drawn in one long cylinder. The top and half of the body can be drawn from one blank, and the bottom half from another, and the two suitably joined. Dents, sharp corners, and all forms of irregularity, in addition to being difficult to enamel, appear aggravated in the finished article, and are, therefore, to be avoided. Turned-over beads are a necessity for maintaining light gauge articles in shape, and are becoming more than ever indispensable with the continuous reduction in weight of metal used. This economy of metal is often more apparent than real, because the best articles must be made with a substantial thickness of metal.

The finest possible result with greatest durability is obtained by using thick metal basis covered by the thinnest possible coating of enamel. The higher the melting point of the enamel the more brilliant and permanent it will be, but its fusibility is often determined by the metal base. With the light gauges often employed it is necessary to use a soft enamel, otherwise the body softens and collapses during fusing.

It is certainly a retrograde step to strengthen beads by wiring the inside of the bead. The extra thickness of material at the one point, together with expansion troubles on heating, spoil the article for enamelling.

The assembling of parts and fixing of attachments such as lips, handles, spouts and knobs may be achieved by riveting, seaming and welding. These attachments require to be of the same gauge as the body for which they are intended. The enamel on a solid knob cannot fuse in the same time as that on a light gauge body, in consequence it remains dull, a further objection being where the attachment is of any size that it may pull the article out of shape during the fusing process. It is almost impossible to cover rivets with enamel neatly, and these have fallen out of use for anything but the heaviest of ware. Seaming is carried out by the aid of press tools, and leaves a very obvious joint, which is difficult to clean for enamelling, difficult to enamel, and frequently not water-tight when completed. One small advantage seaming has is for attaching a base to such an article as a tall jug. It presents a flange upon which the article may stand during enamelling, firing, and in subsequent use, whereas in the case of an absolutely flat bottom marks must appear where it has been supported during enamelling. Where seamed joints do appear they must be absolutely tight to prevent movement of the metal during heating, which would

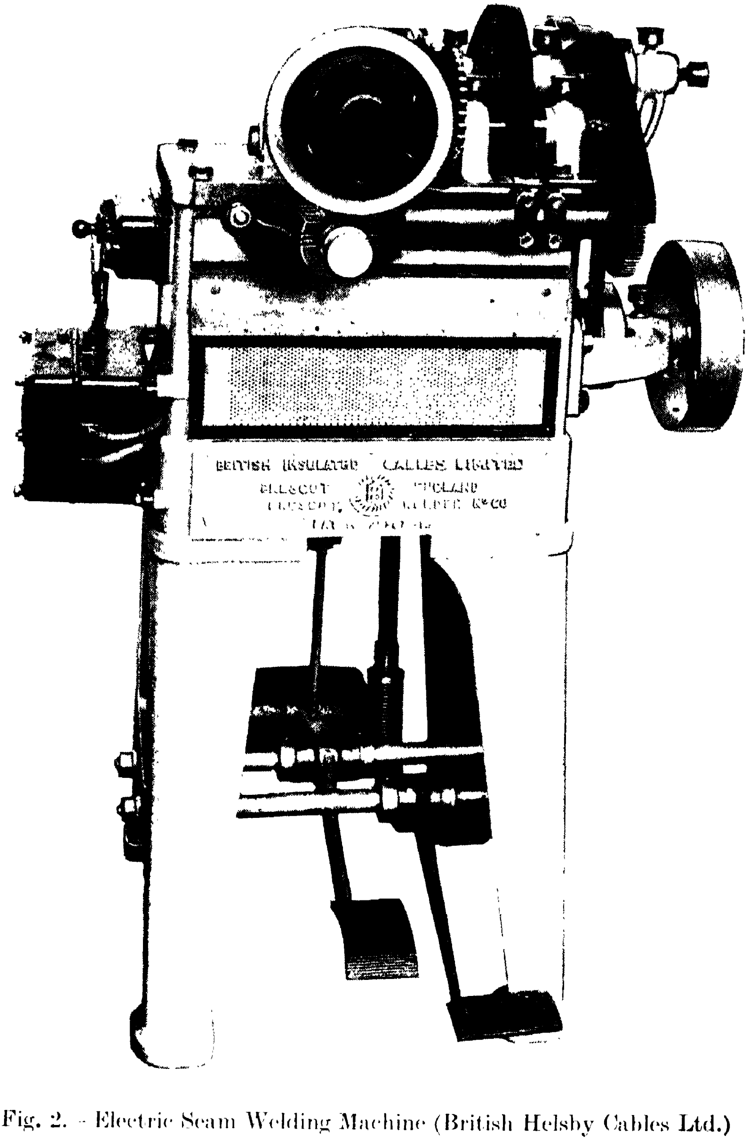

Fig. 2.—Electric Seam Welding Machine (British Helsby Cables Ltd.)

result in a patch uncovered by enamel. A thickness of enamel at this joint will lead to bubbling. The modern process of joining is by means of a weld—that is, melting the two edges of metal, and allowing them to fuse together; the heating may be accomplished either by gas or electricity. The gases employed are either hydrogen burning in oxygen, which gives a temperature of 2,000° C., or acetylene in oxygen producing a higher temperature still, the gases being commercial products available in cylinders. The process of gas welding is of considerable importance for making welds of considerable length—that is, seam welding. For fixing small light articles spot welds by electricity are the best means, and electric seam welding, though more expensive initially, produces a first-class finish. A good weld when covered by enamel should be invisible, and thus a complicated article may be produced in " one piece." It is this desire for invisible welding which has popularised electric welding at the expense of the gas process. As a routine procedure it is virtually impossible to produce the extremely neat and accurate finish necessary, with gas. The process is slow, and the article may subsequently need considerable attention on the lathe or elsewhere to flatten the joint. With electric welding the process is much quicker, simpler, and a better finish is produced. In Fig. 2, a modern example of an Electric Seam Welding Machine is shown, this being capable of operation merely on the touch of the foot lever. The water-cooled rotating wheel electrode is clearly seen (the article to be welded being rotated in sympathy with it), and various jigs and fittings are available for the various classes of work to be handled.

The most common fault in welding is the burning of the metal, leaving small holes, which are visible after enamelling. With gas this may be due to acetylene which is too hot for light gauges, or too large a burner may have been employed; with electric welding it may be due to too much power; both are readily capable of adjustment, but with gas one is very much more at the mercy of the operator than with the electric machine, which is very nearly ideal for routine work. This and the electric spot welder for fixing attachments should meet every call for welding in an enamelling works. The burning of the metal is a common fault with spot welding, the most likely causes being dirty electrodes, or their areas of contact being too large (⅛ inch square is ample), or the operator being too heavy-handed.

Welding, and all the mechanical treatment to which the steel is subjected during shaping, set up strains in the metal which may develop faults in the finished article. A piece of welded metal is shown among the microphotographs, Diagram No. 9. Annealing exerts a normalising action, and this is usually achieved during the cleaning operations which follow. It is sometimes a practice to clean first and then assemble the separately cleaned body, handle, spout, etc. This saves money, by permitting stacking more closely in the tanks during cleaning, and in the consequent handling operations, and should present better work. No further contamination with oil after cleaning can be permitted, and if any of the attachments have to be unduly stretched for welding, it is quite probable that the enamel will part at these areas, as the steel does not become normalised now until it is fired, with the first coat of enamel on it.

For successful enamelling the surface should be soft, spongy and porous, and the articles which give most trouble in enamelling are those which have been subjected to much mechanical treatment. In some cases the stamping and annealing operations force the oil and accompanying dirt right into the pores of the metal. Pure iron has a smoother surface than steel, which is a

Fig. 3.—Cross-Section of Enamelled Steel × 90.

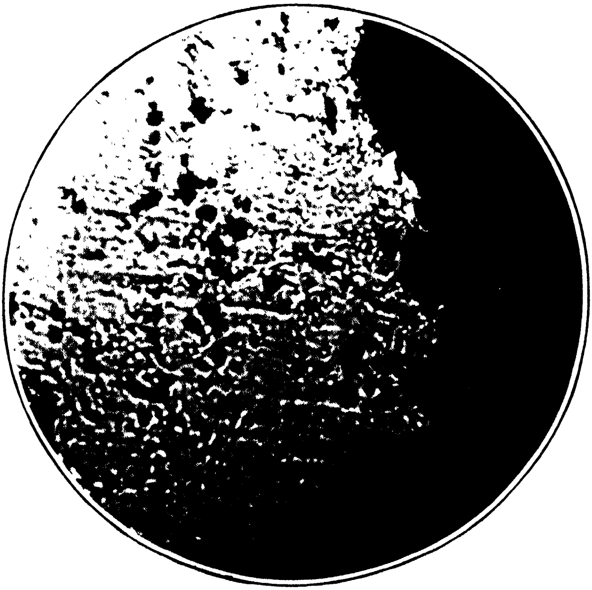

Fig. 4.—Cross-Section of Enamelled Steel × 1,000.

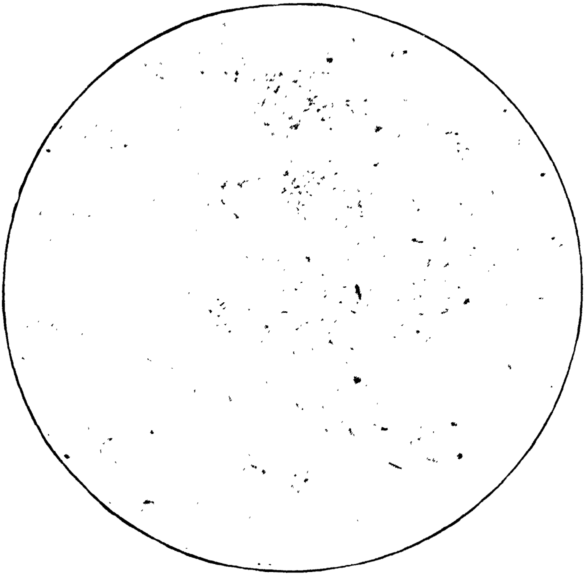

Fig. 5. Pure Armco Iron × 300.

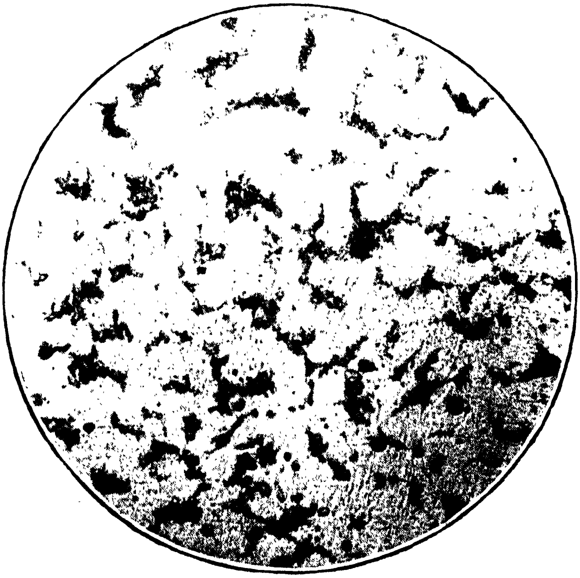

Fig. 6.—0·22 per cent. Carbon Steel × 300.

Fig. 7.—Grey Foundry Iron × 300.

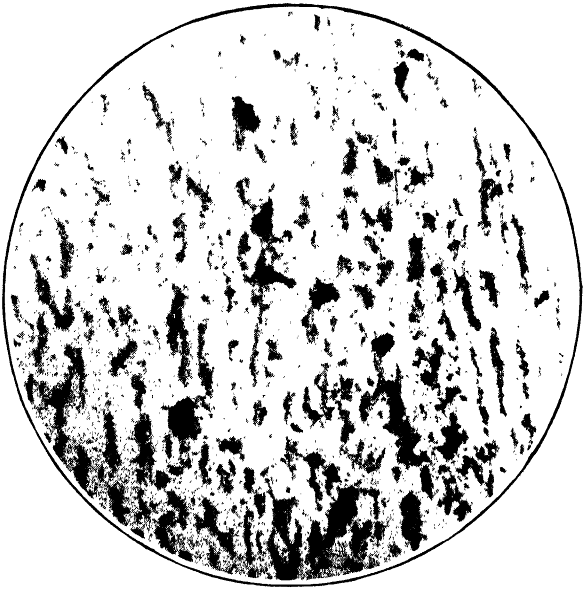

Fig. 8. Dirty Mild Steel × 300.

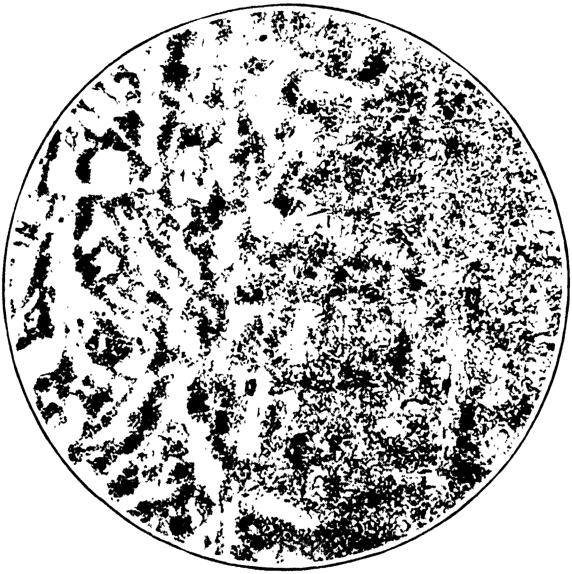

Fig. 9.—A Weld × 300.

disadvantage, but its extremely good drawing qualities and absolute regularity are greatly in its favour. Where beads exist they must be rolled in absolutely tightly, or troubles result from the enamel running in and out; alternatively, they must be definitely open, that they may be cleaned; a half and half bead is worthless.

The Micro-Photographs.

The micro-photographs were obtained at the Wolverhampton and Staffordshire Technical College with the apparatus designed by C. Reichert of Vienna. All specimens were etched, except the pure iron.

Figs. 3 and 4. These represent a cross-section of 27 gauge blackplate enamelled with ground coat only, the first being at 90 magnifications, the second at 1,000. The intention is to illustrate the penetration of the enamel into the steel. In the former diagram the structure beyond the enamel is to be neglected, it representing the solder in which the specimen was mounted. The thickness of the enamel coat is $\frac{1}{10}$th millimetre.

Fig. 5. This is a cross-section of pure (Armco) iron at 300 magnification showing just a trace of carbon, and is intended to contrast with

Fig. 6. A steel containing 0·22 per cent. carbon, at the same magnification. The carbon separates out as iron carbide at the boundaries of the grains of iron. This again contrasts with

Fig. 7, which is a typical grey foundry cast iron magnified 300 times.

The black structureless stalks are graphite; the white areas show the triple eutectic, iron, iron carbide, and iron-phosphide, the alternating black and white being the iron, iron-carbide eutectoid.

The analysis of this cast iron shows :—

Graphite,	3·0 per cent.
Combined carbon,	0·25 ,,
Silicon,	3·0 ,,
Sulphur,	0·03 ,,
Phosphorus,	0·70 ,,
Manganese,	1·00 ,,

Fig. 8. This is a piece of dirty mild steel, the regular streaky nature of the slag inclusion being due to rolling. (Magnification 300.)

Fig. 9. This is a sample from a welded joint, showing the change in structure due to the heat. (Magnification 300.)

Cleaning the Steel.—This is accomplished by heating the metal sufficiently to burn off the oil and grease it has acquired during its mechanical treatment. A film of iron oxide or rust is produced on the surface, which is removed by immersion in acid, the acid being subsequently washed out as far as possible and the remainder neutralised with soda or lime, and the article quickly dried. The whole process may be eliminated and sand blasting substituted—that is, the mechanical removal of the outer layer by finely powdered sand being forced against the surface. This is the usual process for cleaning cast iron, and large steel articles, but it is too expensive for the usual class of sheet steel samples. It presents a surface well suited for enamelling, and produces excellent results.

The removal of grease by heating is generally classed under two headings, grease burning, and scaling, the distinction being that in the former case the article is heated to a temperature just sufficient to burn off all the grease, about 650°, whereas for scaling slightly higher temperatures prevail, and acid is used with the furnace load. This latter process is advisable in the case of old and well rusted samples, and causes the oxide to flake off and leave an easily cleaned surface. The type of furnace used is generally of the muffle or semi-muffle type, but may be advantageously replaced by a long cylinder heated in the centre—that is, a tunnel furnace similar to that used for glass annealing. The ware may then be fed automatically at one end, and withdrawn when cool at the other; this ensures gradual cooling, which is necessary for annealing. A good current of air is essential to the burning, and as a furnace rapidly becomes choked with fumes from the oil, these may be removed periodically by throwing in limestone. At a low temperature this decomposes into quicklime and carbon dioxide (carbonic acid gas), which clears the furnace of fumes, and incidentally the lime is useful in removing the acid fumes after scaling.

Both under-burning and over-burning are to be avoided, as a hard surface of oxide remains which is difficult to remove subsequently. In the case of simple shapes which have undergone little mechanical treatment, and where little oil has been used, it is possible to eliminate grease burning altogether and to substitute immersion in a hot caustic soda solution, or some similar proprietary preparation based upon it. This procedure takes but a few minutes, and the success or failure of it depends entirely upon the grease with which the steel has come in contact. Caustic soda decomposes the fatty oils (that is, animal and vegetable oils such as castor oil), and dissolves the resulting products, and a certain amount of mineral oil (that is, petroleum products) will be removed by the formation of an emulsion, but if the proportion of mineral oil is too great, failure is certain. Where the stamping operations are under control, and no new oil can be inadvertently introduced, the process is an economy, but any error may cause extensive trouble.

Pickling.—Whichever course is adopted, it is followed by immersion in acid. Two acids are available, sulphuric acid and hydrochloric acid (trade name, muriatic), and a third substance, nitre cake, is worthy of mention. This last is sodium bisulphate or sodium acid sulphate, a by-product from the manufacture of nitric acid, and being a solid shipped in bulk, is low in price, this constituting its chief virtue. In water it behaves like a mixture of sulphuric acid and sodium sulphate, and, of course, the acid is the active principle.

Thus :—

$$2NaHSO_4 \rightarrow Na_2SO_4 + H_2SO_4.$$

Sodium bisulphate → sodium sulphate + sulphuric acid.

It requires to be used hot, and must obey all the conditions required with sulphuric acid.

Sulphuric acid in concentrated form is not a pleasant liquid to handle, and when diluted with water generates appreciable heat ; the acid must be added to the water in small quantities at intervals, the reverse procedure leading to dangerous spurting of hot acid. For pickling it must be used hot, when objectionable fumes are generated, but weight for weight it is cheaper and more effective than hydrochloric acid, and is the usual choice of manufacturers employing large sheets, where there is little handling to be done. For hollowware, and the small enamellers generally, hydrochloric acid is highly preferable ; it may be used efficiently in the cold condition, generates few fumes, and is simpler in many ways. Furthermore, cold hydrochloric acid dissolves less iron oxide than hot sulphuric acid, which is an advantage.

Hydrochloric acid comes on to the market as a yellow liquid, slightly denser than water (sp. gr. = 1·16 to 1·18). The actual acid is a gas, hence the commercial product is a solution of it in water. The colour is due to iron impurity, the pure solution being water white. The highest strength obtainable is 39 per cent., the commercial acid ranging about 30 per cent. Hence if 1 part of this is diluted with 2 of water, the strength recommended for pickling operations, a 10 per cent. hydrochloric acid is being used. The acid is generally transported in large glass carboys containing 1 cwt. each, but these being fragile are a constant source of worry, and should be excluded from the works, the acid being stored in a tank of acid-resisting brickwork, or other material, and pumped as required. A variety of materials is available for the manufacture of the pickling tanks; stone, which is heavy and readily chipped, brickwork which generally presents a large number of joints, acid-resisting metals, and woodwork. The last-named has been found to be the most economical. Good, well-seasoned pine with tightly fitting joints, held together with acid-resisting rods and bolts, satisfactorily meets the case. A double tank may be used and the two interlined with lead or pitch, but a coating of the latter on a 2-inch tank is usually sufficient to produce a liquid-tight vessel of good durability.

The articles to be pickled must be completely immersed in the acid, and some form of agitation employed, since the removal of the scale is mechanical and not chemical. Burnt iron oxide is not readily dissolved by dilute acids, but these on coming into contact with the metallic iron, start dissolving it and evolve hydrogen, which forces off the outer layer of scale. This conclusion is confirmed by C. A. Edwards,* who, among other technical

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* *Journ. I. and S. Inst.*, Sept., 1924.

considerations, states that the hydrogen is absorbed by the metal, rendering the latter brittle; also that the hydrogen diffuses right through the steel and exerts a pressure at the opposite face, sufficient to remove a coat of enamel. It may be advisable to remove most of the scale with a wire brush before immersion, it generally flakes off readily, but if this is not done, it merely leads to a bigger deposit of scale in the bottom of the tanks, and does not appreciably affect the strength of the acid. No definite time can be laid down for pickling, it depends on too many factors, such as the nature of the blank, and strength of acid employed. This latter should be 10 per cent. actual acid to commence with (one of strong acid to two of water), and should be abandoned when the strength falls below 5 per cent. It is advisable to use a little of this old acid in place of water when making up new solution, since a small quantity of the dissolved iron improves the working. A plain simple shape may be simply wasting iron and acid after twenty minutes' immersion, whilst seamed articles may require hours. Where overhead transport facilities exist, the tanks may be arranged in a counter-current system—that is, the raw articles thick with scale immersed in the weak and nearly exhausted acid, and then after this preliminary treatment immersed in stronger acid to complete the cleaning. This extra handling is beyond consideration where hand labour would be necessitated.

There are many substances available for economising acid; they are either derivatives of organic acids, formaldehyde, or certain sugars, and have the property of limiting the attack of the acid on the iron. They are generally sold as proprietary articles under trade names at considerably above their value and disguised by inactive ingredients. Undoubtedly they save acid, and are worth using. When used, no bubbles of hydrogen are visible.

Washing.—The articles should be transferred immediately from the acid to water, and no more delay than is necessary for the first runnings of acid to separate should be permitted. The practice of allowing articles to drain completely cannot be tolerated ; an iron article wet with acid will rust immediately in air, and all the work of pickling is undone. Running water would perform the washing more effectively ; it gradually becomes a weak acid solution, but a difficulty which this presents will be mentioned later. The last traces of acid are removed, and an anti-rust surface produced by immersion in an alkali. The usual practice is first to use a tank containing cold strong soda, and finally one containing hot dilute soda, this procedure being adopted to leave the article with the minimum amount of soda attaching to it. The former tank may be substituted by slaked lime, which is cheaper, but this is not so soluble and forms a sediment at the bottom, requiring stirring, preferably by means of live steam. Lime cannot entirely replace soda, because a coating of lime would readily take up carbonic acid gas, forming calcium carbonate, with consequent trouble later. From the final soda tank the ware is dried as quickly as possible and examined. The work should possess a dull, clean-looking, grey surface, and by no means a bright, silvery appearance ; the latter indicates an insufficiency of soda, and the ware will quickly tarnish. The strength of soda solution is in the neighbourhood of 1 per cent., and when approaching saturation it frequently leaves brown stains in the work, due to the iron compounds carried over from the washing water. The soda tanks should be made up fresh daily.

A series of tanks is thus required for the cleaning operations, the various units containing respectively:—

(1) Acid	or	(1) Weak acid.
(2) Water		(2) Strong acid.
(3) Strong cold soda		(3) Water.
(4) Weak hot soda		(4) Lime water.
		(5) Hot dilute soda.

No special precautions are necessary in the construction of the tanks for water and soda ; wood is generally selected for the former, and iron for the latter, the chief necessity being water-tightness. Where wood is employed it is essential, of course, that the tanks be kept wet always, to prevent warping. Where sulphuric acid is employed it is necessary, and with hydrochloric acid it is advisable, that an adequate draught system be employed to remove the fumes.

The maintenance of the cleaning solutions at their correct strength is an important consideration, and should be attended to daily. This applies particularly to the acid, where time and money are frequently wasted by trying to use exhausted solutions, or by their disuse before they have lost their activity. The absolute determination of the amount of acid left in a bath is work for a chemist, as its analysis is complicated by the presence of the dissolved iron. Many expedients are available for obtaining a figure of sufficient accuracy for practical purposes, and these are often the subject of patents. One of the simplest available methods comprises a cylindrical jar shown in Fig. 10, having an index line A in red, and graduated above by marks 1 to 10 or 15. The acid to be tested is filled up to the line A, and caustic soda solution of known strength is added a little at a time, followed by thorough shaking, until a thick green grey deposit forms. The mark on the jar is then read off, and this corresponds to the percentage of actual acid present. After a little practice the method is perfectly simple, quick to execute, and quite reliable, and may be performed by the pickling foreman. The only requirement is normal caustic soda solution, which may be obtained from most pharmacists. The strength of the soda solution may be determined by direct treatment with acid.

Pickling may be greatly accelerated by passing a suitable electric current through the ware and acid. This process, known as electrolytic pickling, is also claimed to save acid, and obviates the necessity of stirring. The ware to be pickled is attached to one pole of the battery, and the other electrode is either inserted in the pickling cage or the tank acts for the purpose. So far electrolytic pickling has not been adopted to any extent commercially.

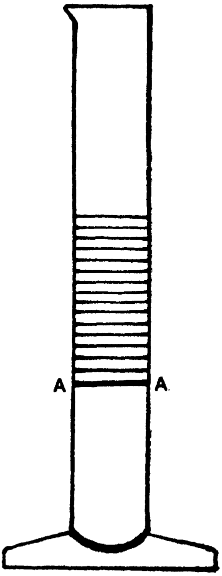

Fig. 10.—Graduated Jar for Testing Strength of Pickling Acid Solutions.

The quantity of liquid being handled necessitates sloping floors and adequate drainage. The floor also should be of a good resistant material, such as Staffordshire blue brick. The disposal of the waste liquors requires serious attention since it is illegal to pass objectionable materials such as acids, alkalies, or iron salts into public sewers. Where hydrochloric acid is used the products of pickling will be a solution of ferrous chloride, and with sulphuric acid, ferrous sulphate. In the former case the waste pickle will include ferrous chloride, weak acid (since this cannot be completely exhausted), and iron oxide. This liquid will attack and destroy the joints in the sewers, and eventually, when reaching the outfall works, will interfere with the sewage disposal. The dissolved substances will require treatment with lime, and subsequent sedimentation and transport to a dumping ground. The treatment with lime may be partly obviated by using the waste soda from the cleaning tanks at the works for the purpose, but the sludge formed has still to be dealt with, and may be a charge against the manufacturers. The importance of this problem may be more obvious when it is realised that 1 ton of hydrochloric acid produces $1\frac{3}{4}$ tons of ferrous chloride, which require 1 ton of lime for treatment, and produce 60 tons or so of sludge (since the sludge obtained contains only about 2 per cent. solid matter). It is thus advisable to develop some means of treating these pickling residues. The exhausted pickle may be separated from the solid deposit and evaporated to dryness, when ferric chloride will be obtained from hydrochloric acid pickle, since ferrous chloride readily oxidises to this in air, or ferrous sulphate from sulphuric acid. These both have a commercial value, more particularly the latter, though generally speaking neither will be found to pay for the expense involved, but it may possibly happen that a local demand for the material exists. Iron oxide which may be recovered from the deposits in the tank finds employment largely in the paint industry, but a simple calculation will show that a good-sized pickling plant will produce enough iron oxide to supply the whole paint industry, hence the supply greatly exceeds the demand, and again a worthless product has to be dealt with. Where no such means of disposal is available the simplest plan for a large works is to follow the Continent's example and instal its own settling tanks, where it treats its own waste pickle with lime, the sludge being pumped on to waste land.

Drying and Examination.—It is essential after cleaning that the blanks be dried quickly and covered with enamel without delay. Waste heat from the furnaces may be employed for the drying, or special stoves designed, a temperature approaching 200° C. being required. When steam is employed for heating the cleaning tanks the same system may be used for a drying stove, and in the larger plants it is customary to combine this stove with a conveyor to the enamelling department, the stove being fitted with a slow-moving endless belt for the purpose. The speed and temperature are such that a wet article placed in one end is dry and cool enough to handle on its arrival at the remote end. The belt requires to be well mounted for smooth running, otherwise damages result to the ware which more than compensate for any convenience obtained.

On passing from the cleaning to the enamelling department the work requires to be strictly examined, for faults at this stage produce wasted finished articles which are beyond redemption and only fitted for the scrap heap. The inspection should be carried out by an experienced man who will ruthlessly return all but perfect work. He may combine with this work the removal of any dents or other deformations by means of a wooden mallet and suitably shaped formers. Some dents are so small as to be only visible when the surface is damped, but these must be eliminated, as they are quite prominent in the finished ware. This work should be done at least by semi-skilled labour, but is often eliminated on the ground of being a non-productive outlay, but the system is retained by the best works, and is becoming more than ever necessary with the ever lightening of the gauge of metal employed.

Because of their unpalatable nature, pickling and cleaning are generally done in some out-of-the-way part of the works, and often for the same reason fail to receive the close supervision necessary for success. Without a clean foundation, successful enamelling is impossible.

CHAPTER II.

THE GENERAL PROPERTIES OF ENAMELS.

Enamels considered chemically, are essentially glasses —that is, complex alkaline boro-silicates, usually containing fluorine, and are produced by mixing and melting such materials as borax, soda, felspar, cryolite, and quartz. Enamelling is thus a branch of the ceramic industry, and consequently closely associated with china, earthenware, glass, and pottery generally, the term ceramic being applied to that large class of chemical compounds known as silicates. The coating applied by the potter to his ware is simply an enamel of high melting point, and requires about as many days to fuse as an ordinary enamel requires minutes. True enamels must be applied by heat, and this reduces the choice of materials enormously, the selection being limited to those substances capable of withstanding a temperature of 1,000° without destruction. This restriction is mainly felt in coloured enamels, where the manufacturer is debarred from using the beautiful and extensive range of colours available to the painter and dyer. A further restriction in the case of domestic ware is the abolition of all materials which might possibly be detrimental to health, and the wider use of enamelled ware may undoubtedly be attributed to its harmless character.

The fundamental constituent of an enamel is the root of all ceramics—namely, silica—and this enters the enamel in one or more forms, such as quartz, flint, sand, felspar, and the more recently employed sodium silico-fluoride. The simplest conceivable enamels are the product of melting sodium carbonate with quartz, the soda being necessary to lower the melting point of the quartz to within practicable limits. The temperature of the melting point may be altered at will by varying the proportions of the two constituents. There are many objections to an enamel composed entirely of the product from melting soda with quartz, two of the more obvious being that the sodium silicates produced are soluble in water, and that their expansion and elasticity would not enable the enamel to be successfully applied to and retained by the iron surface, hence the numerous other ingredients which find employment in the industry. The necessity for melting is in the production of the most intimate possible association of all the ingredients, the rendering of substances soluble in water insoluble, and infusible substances fusible.

The Requirements of Enamelled Ware.—The primary service of enamel to-day is one of utility, the protection of an iron or steel surface from rusting, the final article possessing the strength of steel, and the appearance of chinaware, combining the advantages of portability and unbreakability with resistance to direct heat and corrosive action. The qualities expected from enamelled ware, then, are diverse, especially where domestic ware is concerned, and include ability to withstand shocks such as being let fall, sudden changes of temperature through being heated until contents have gone dry and the body is red hot and then sudden immersion in cold water. The appearance must be clean, hygienic, it must not taint food, nor itself be dissolved by the acids of foodstuffs during cooking. Its treatment during manufacture demands that the enamel shall expand and contract with iron—that is, minerals which generally have a low expansion shall be made to work in sympathy with metals which are notoriously high in expansion. The "man in the street," on being told that the problem facing the enameller is the application of a sheet of glass to a sheet of iron to produce a durable combination, would remark that it is attempting the impossible. So great has been the success, and these high ideals have so nearly been reached that an ever-increasing demand for enamelled ware is experienced, and its applications steadily expand. For domestic ware it offers many advantages over its competitors, on the grounds of economy, less weight, and unbreakability over china, again economy over nickel ware, and the new stainless steel articles, whilst aluminium, which is the chief competitor, is limited in use, its light weight and conductivity of heat being too good for some cooking utensils, allowing their contents to burn. Aluminium has a poor resistance to soda and salt solutions, and is not so easy to clean as an enamelled surface.

For heavy domestic work, and wherever vessels of large capacity are required, cast iron is employed as a basis, and for special work such as chemical manufacture large cast-iron pots covered with special acid-resisting enamels are employed and are found to give excellent service, their manufacture forming an important branch of the industry.

Constitution of Enamels.—The raw materials of the enamelling industry are principally commonly occurring minerals, such as felspar, quartz, and clay, which after a certain amount of rough purification are ready for use, whilst others, like borax and soda, though found to some extent in nature, are generally manufactured from more abundant raw materials. Oxygen is the most abundant element occurring in the earth's crust, hence many of the naturally occurring minerals are compounds containing oxygen, and are known as oxides. The next two most commonly occurring elements are silicon and aluminium, and these three elements together with metals in various combinations constitute in the main the earth's crust. A vast portion of this is the conglomerate granite, which contains the mineral felspar, a compound of the metals potassium and aluminium, with silicon and oxygen, which is of fundamental importance in enamelling. The oxides introduced into enamels serve one of three purposes, (*a*) they melt comparatively easily and are known as fluxes, (*b*) they have the reverse action, are difficult to melt, and are known as refractories, or (*c*) they are employed to introduce colour, which term includes the use of opacifiers to produce whiteness in white enamels. Generally speaking, the oxides of the metals act as fluxes, and those of the non-metals such as silicon and boron as refractories. Sodium and potassium are known as the alkali metals, and their oxides constitute the major part of the flux portion of an enamel. From the foregoing definitions aluminium oxide would presumably be a flux, whereas it is one of the most refractory substances known. Chemically, it is capable of acting both as a metallic or non-metallic oxide, and in enamelling its position is one of peculiarity, which feature is enlarged upon in Chapter VI.

Comparison with Metallic Alloys.—To understand the constitution of enamel or glass it is useful to consider the metallic alloys. An alloy is an intimate mixture of two or more metals made by mixing them together whilst molten, and presents an absolutely homogeneous appearance. Although certain pairs of metals cannot be made to mix together in all proportions while in the molten state, these are exceptions, and in the vast majority of cases any two molten metals can be mixed in any relative proportion. In this respect these fluids resemble such mixtures as alcohol and water. What happens to the mutual solution of the two metals when the temperature is lowered so that solidification sets in ? In certain cases the state of mutual solution remains undisturbed, and each of the crystals which are formed ultimately, possesses the same average composition as the molten liquid from which it was deposited. Such crystallised solutions are termed "Solid Solutions."

Glass is defined as a homogeneous mixture, and not a chemical compound, because a compound in addition to being homogeneous must have its constituents always united in the same definite proportions. Glass obeys the former, but not the latter, for in the case mentioned above soda and quartz may be melted together in almost all proportions to form a glass, but only in two or three definite proportions to produce sodium silicates which are chemical compounds. For our purpose we may regard glass as a solid solution, though it is a fine point chemically, which is receiving the close attention of research workers, whether glass is a true solid solution or another form of combination. Enamels are described as vitreous enamels, because of their ability to form glass-like solids on cooling from the molten state, and the fault occasionally found in enamels known as devitrification, causing dull porous enamels, is due to one or more ingredients in the enamel crystallising out on their own instead of as a part of the whole glass. This fault is likely to be produced by maintaining the enamel at a temperature just below its melting point for some time, or by slow cooling, such as cooling in air instead of the usual immersion in cold water.

A further similarity existing between metals, glasses, and enamels, is the influence of the presence of one substance on the melting point of another. Generally the addition of a small quantity of one substance to another pure one results in a lowering of the melting point.

Pure silver melts at 960° C., pure copper at 1,084° C. ; if a little copper be added to silver, the new melting point, instead of being higher than 960° C., is lower, and the temperature may be continuously reduced by further additions of copper until an alloy consisting of 28 per cent. of copper and 72 per cent. of silver is obtained ; this melts at 770° C. ; any further addition of copper now raises the melting point. Again, if silver be gradually added to copper, the melting point of the latter

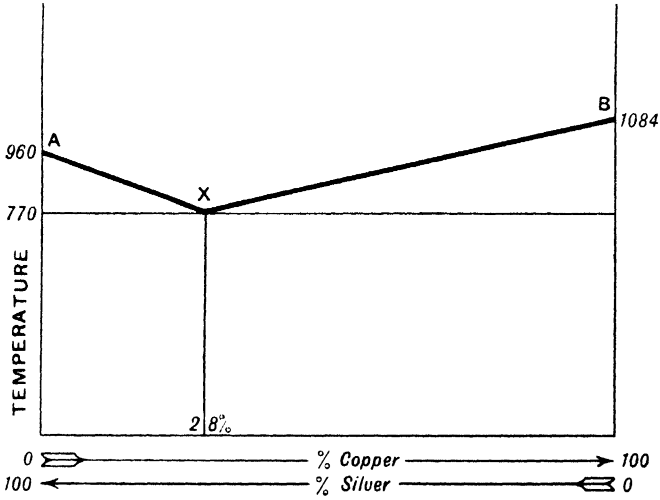

Fig. 11.—Diagram of Copper-Silver Alloy.

may be steadily lowered from 1,084° to 770° C., when the composition of the alloy is as above. Any addition of copper or silver to this alloy raises the melting point. It is, therefore, the lowest melting alloy of copper and silver, and to this composition is given the name EUTECTIC, from the Greek, meaning "easily melted." This is shown in Fig. 11, the proportions of copper and silver being shown along the horizontal, and temperatures being marked up the vertical ordinate O A. An alloy containing 100 per cent. silver and 0 per cent. copper—

that is, pure silver—melts at the point A; additions of copper lower the melting point, which falls continuously along the line A X, after which it begins to rise again to B, when the composition of the alloy is 100 per cent. copper and 0 per cent. silver—that is, pure copper. The point X corresponds to 72 per cent. silver and 28 per cent. copper, and the melting point is 770° C.; this is the eutectic mixture for copper and silver. This ability to produce low-melting mixtures is not confined to two metals, but three, four, or more, may produce a eutectic; in fact, one of the best-known examples is Wood's metal, which contains four metals in the following proportions:—

Bismuth, ...	4
Lead, ...	2
Tin, ...	1
Cadmium, ...	1

This alloy melts at 71° C.—that is, well under the boiling point of water—whereas none of the individual metals melts under 230° C. Neither is this property confined to metals, but is a characteristic of enamel ingredients also, and this explains why it is possible to lower the melting point of an enamel by the addition of a high melting substance such as quartz. The first conclusion with such a freakish happening transpiring would be that a mistake had been made in the materials used, but it may be explained by the formation of a eutectic. Quartz melts at 1,660° C. and alumina at 1,880° C., yet the addition of alumina to quartz up to 9 per cent. may reduce the melting point 150° C. Whilst much investigation work has been done on these eutectics of interest to enamellers and glass makers, it is idle to suggest that our knowledge is complete or that except in a few simple cases it is possible to predict a lowering in melting temperature by the addition of a refractory substance.

Silica has been mentioned as the fundamental ingredient of enamel, and also as the typical refractory, soda being taken as the typical flux, the higher the proportion of flux the lower the melting point of the enamel (or in trade usage the "softer" it becomes). The bulk of the silica is seldom introduced from raw quartz, but rather from felspar, which consequently becomes an ingredient of prominence. In addition to containing silica, felspar yields the flux potassium oxide, and alumina, the oxide of aluminium, and is in fact the main source of alumina, since this material cannot be introduced as such in an enamel, because it does not flux readily with soda, and would remain infusible. Felspar thus typifies an enamel. It contains flux, refractory and alumina, which is necessary as a "go between," and is useful, since it helps an enamel to adhere well to iron, and during cooling after the ware has been fused, slows the process down, and prevents cracking and chipping. Felspar melts about the same temperature as enamel; in fact, a good rough and ready test for it is to try a small heap of it in a melting furnace. It should fuse and produce a white, glossy, opaque mass, and any discolouring matter, or infusible impurity, will be readily obvious.

The third class of substance introduced into an enamel—namely, that for the production of colour—consists mainly of metallic oxides which possess the necessary colour qualification. For white enamels, the opacifying agents belong to either of two classes, ultimate opacifiers or partial opacifiers. The first are again metallic oxides, and since their power is greatly diminished by prolonged heating with fluxes, they are added to the remainder of the enamel after this has been melted. The partial opacifiers are mainly compounds containing fluorine, the commonly used substances being cryolite and fluorspar, and these being also fluxes are melted with the enamel. The molten enamel from the furnace is generally cooled suddenly by running into cold water, producing the so-called frit (from the German "fritt"), which comprises very friable crystals. Sheet steel enamels being always applied to the metal in liquid form, these crystals are ground with water. Frits which have not been quenched are very tough, and require special treatment. The slop enamel consisting of the finely ground frit in water is not very serviceable in this form, as the powder immediately settles to the bottom, with clear water above, hence a further addition is necessary to maintain the enamel in suspension, and as clay possesses the ability to do this, in addition to introducing two valuable ingredients in silica and alumina, it is the material employed for the purpose.

The various raw materials are now discussed in detail, following which their influence on the characteristics of the final enamel are dealt with. The physical properties dealt with include the effect on expansion, elasticity, melting point, resistance to air, water, and acids, and durability.

CHAPTER III.

RAW MATERIALS USED IN FRIT MAKING.

THE raw materials commonly used in enamelling are considered in this, and the two following chapters. This chapter is confined to those materials which pass through the melting furnace, and are thus used for frit making. Where the same ingredient is used for more than one purpose, it is considered under the heading dealing with its more important use, the necessary cross-references being given to facilitate its being found. In this chapter the materials are dealt with alphabetically, and in general the origin is given, enough of the manufacture to indicate likely impurities, the limitations of use, the function in the enamel batch, effect on the finished ware, costs, and simple tests for purity. The meaning of the formulæ and molecular weights (M.W.) given, is explained in Chapter VI.

Alkali.—*See* sodium carbonate.

Alumina.—Aluminium oxide, Al_2O_3, M.W. = 102. An essential ingredient of enamels, but never introduced as such, as it is infusible, and would not be absorbed in the enamel. It finds employment at the mill as a hardening agent, and it is used for diluting the prepared colouring oxides.

Ammonium Carbonate.—Composition somewhat indefinite. Finds employment principally as a mill addition (see Chap. IV.). It is, however, advocated for inclusion in the batch for melting. At the furnace temperature it leaves no residue, hence its weight is a dead loss. It is claimed that if used up to 3 per cent., on volatilising it bubbles through the batch, opening it up, and allowing easier and better melting.

Antimony Oxide, Sb_2O_3, is used almost exclusively as a substitute for tin oxide (see Chap. V., p. 91), always being fritted with the enamel. It finds a limited use in ground-coat enamels containing no cobalt.

Artificial Cryolite.—*See* sodium silico-fluoride.

Barium Carbonate.—$BaCO_3$. M.W. 197. M. Pt. 1,360°. A heavy white powder. On ignition passes to BaO, hence loss = 22·3 per cent. It is found in nature in Northumberland as the mineral *witherite.* The M. Pt. indicates that it is difficult to fuse, yet when it is incorporated in the batch, it enables it to fuse on to the iron more easily. It does not materially affect the expansion or elasticity of the enamel. It may be used as a partial substitute for soda, up to 5 per cent. being used, but its most important use is as a substitute for lead in the production of leadless enamels, hence it is of little interest to the sheet-metal enameller. It produces a high lustre, and like lead permits of a low melting enamel being obtained, though in excess it is liable to cause devitrification. Although it is undoubtedly less poisonous than lead, there is some controversy whether it is absolutely free from danger, as it is used as a rat poison. For enamelling, the crude mineral is never used, but always chemically prepared barium carbonate, which may be produced from *witherite* or *heavy spar* (barium sulphate). In this latter case care must be taken to remove all sulphur, otherwise in the process of enamel production barium sulphate, $BaSO_4$, may be re-formed, producing dull white patches or blisters. Barium carbonate contaminated with sulphate may be readily detected by treatment with hydrochloric acid, when it should completely dissolve. A heavy white residue should cause the sample to be rejected. Possible impurities include sodium carbonate, sulphate, chloride, magnesium and calcium salts. One sample which came under the author's notice contained 50 per cent. barium sulphate.

Borax.—$Na_2B_4O_7$, $10H_2O$. M.W. 382. This is used in three forms, white crystals at about £21 ton, granular at about £20 ton, and borax glass, $Na_2B_4O_7$, M.W. = 202. Borax melts in its own water of crystallisation. It is manufactured from boric acid, which occurs naturally in the lava from volcanoes, especially in Tuscany, simply by treatment with soda. Borax usually appears on the market in a high state of purity, exceeding 99·5 per cent. Foreign matter can be discovered by shaking with water, when a clear solution should be obtained. Possible impurities include sodium carbonate, sulphate, chloride, magnesium and calcium salts, and it is sometimes adulterated with alum and salt. The most likely adulterant is soda, and this may be detected by treating the sample with dilute acid, when any soda present will cause effervescence. There should be no turbidity on the addition of alkalies or silver nitrate. Sulphate is tested for by the addition of barium chloride, which throws down a heavy white precipitate of barium sulphate insoluble in hydrochloric acid. To detect chloride, dissolve in water, add dilute nitric acid and silver nitrate ; a white precipitate, darkening on exposure to light, and soluble in ammonia, proves chloride present.

Being the lowest melting substance present, borax is the most active flux. It gives strength to an enamel, and a brilliant lustre which cannot be produced in its absence. It may be used up to 35 per cent. in ground-coat frits, and 30 per cent. in white. Any increase of borax at the expense of soda will have a reducing effect on the expansion, causing the enamel to chip readily, and lowering its resistance to the attack of fruit acids.

Borax is a useful addition where crazing is happening, but renders an enamel more transparent. The composition of borax crystals is represented by—

Sodium oxide,	16·3 per cent.
Boric oxide,	36·6 ,,
Water,	47·1 ,,

the water (nearly 50 per cent. by weight) being lost before any chemical action takes place in the furnace. The original price is above the average cost of enamel ingredients, and when it is taken into consideration that 50 per cent. is lost, excessive borax soon renders an enamel expensive.

(The further use of borax as a mill addition is discussed in the next chapter, and further commented upon under Grey Enamel, Chap. VIII., p. 153.)

Boric Acid.—H_3BO_3. M.W. 63. Price about £35 per ton, varying with the price of borax. This usually appears as a fine white crystalline substance of high purity, and is used in frits when the boric oxide content is required without the addition of alkali. When the proportionate amount of sodium carbonate is added, borax is produced, though this is not a commercial proposition to the enameller, and the same effect is not obtained in the enamel batch, the boric acid melting before the soda. On heating it loses water and produces boric oxide, the loss on 100 parts being 43·5 per cent. The composition is represented by—

B_2O_3,	56·6 per cent.
H_2O,	43·5 ,,

It gives lustre to an enamel and reduces crazing. It is volatile in steam, and with fluorine compounds yields the gas boron fluoride. It is less soluble in water than borax.

In Chap. IX., p. 138, some interesting examples are given of the effect of boric oxide on metallic oxides, and it is for this reason that boric acid finds employment. It is useful in coloured enamels up to 10 per cent., because it develops the colour in a manner that borax does not, while for other purposes it may be replaced by the cheaper borax.

Calcium Carbonate.—$CaCO_3$. M.W. 100. Known also as *calcspar, limespar, limestone, whiting, Iceland spar, calcite, marble and chalk.* Price about £4 ton. It is a white powder, used solely as a frit constituent. Lime compounds are useful additions to the enamel batch when used sparingly, 5 per cent. being the limit, but 2 per cent. the most usual amount, as they prevent frothing. Lime is more usually introduced in the form of *fluorspar*, but when fluorine is not required, the carbonate is used. At the heat of the furnace it gives off carbon dioxide to form quicklime, the loss on ignition being 44 per cent. An excess of lime gives a dull finish, and tends to cause devitrification. Lime acts as a flux, partially replacing the more expensive soda. It does not flux readily at the batch temperature, hence it tends to raise the melting point, but when once it is incorporated it reduces the fusing temperature of the enamel, which may be an advantage, but narrows the burning range. Hence careful fusing is required. It does not materially affect the expansion or elasticity. It is more popular in American practice.

Calcium Fluoride, *see* fluorspar.

China Clay, or *Kaolin,* Al_2O_3, $2SiO_2$, $2H_2O$. M.W. 258. The general properties of clay are considered in the next chapter, p. 66. China clay is used in small proportions as a cheaper source of alumina than felspar or cryolite, when no extra flux is required. The price of a good quality is £3 a ton. The principal source of the material is the mines of Cornwall, where the material appears in white or slightly tinted soft lumps. Enamelling can only absorb a very small portion of this output, the bulk going for china manufacture, other uses being as a filling for paper, tooth-paste, etc. High-grade china clay is the purest clay known; it possesses moderate plasticity and a high heat resistance, the softening point being higher than 1,700° C. Geographically, it is secondary clay, but it is usually found near the original deposit, and after the removal of coarse particles it is generally in a high state of purity. Ignited china clay is sometimes added to the mill purely for hardening, but fritting with the enamel is more customary. On ignition it only loses water to the extent of 14 per cent. Where white enamel is being made white burning clay is essential. It is used only in small proportions up to 2 per cent., and must be broken up and sieved through at least a 20-mesh sieve, and thoroughly mixed with the flux to prevent it balling together on top of the batch in the melting furnace and becoming infusible. A bigger proportion will adversely affect the lustre, and cannot be recommended, though its low price and resistance to corrosive liquids make it attractive. The most likely impurities are quartz and carbonates, which may be detected by giving an effervescence with acids.

Chromium Oxide.—Cr_2O_3. M.W. 152. This usually appears as a green powder, though other coloured samples are known. Its sole use is as a green pigment, for which purpose it may be added at the mill or fritted. In the former case it is difficult to incorporate, as it is not readily fusible (M.P. in the neighbourhood of 3,000° C.), hence fritting is recommended, up to 5 per cent. being used, when brilliant greens are obtainable. It is insoluble in water and not readily dissolved by dilute acids. Excess of soda in the frit will produce yellow sodium chromate, which will dissolve out. Though not so striking in effect, chromium oxide is to green what cobalt oxide is to blue, and has been used throughout the ages as a green pigment for glass or pottery. The colour is unaffected by the oxidising or reducing atmosphere of the furnace. Chromium oxide is obtained from the mineral *chrome ironstone,* from which it is separated from the iron by fusion with alkalies and extracting the yellow alkali chromate with water. The green chromium oxide is obtained by ignition with sulphur. It is important for our purpose that all alkali and sulphur be removed. It has a favourable effect on the expansion and no loss on ignition. Its price is about 1s. lb. See also p. 176.

Chiolith.—$Na_3Al_2F_4$. M.W. 199 (Vielhaber), or
$Na_3Al_3F_8$. M.W. 348 (Grünwald).

This must not be confused with cryolite, which it resembles, and in conjunction with which it occurs naturally in the Urals. It is one of the newer enamelling materials, but has so far attained little prominence, though its supporters claim for it greater opacifying power than that possessed by cryolite.

Cryolite.—Na_3AlF_6. M.W. 210.

Its composition may be represented by :—

NaF, . .	60 per cent.	or	Na_2O, .	44·3 per cent.
AlF_3, . .	40 ,,		Al_2O_3, .	24·3 ,,
			F, . .	54·3 ,,

This occurs naturally and is found only in Greenland, usually in a very pure state, though it may contain up to 5 per cent. of quartz. It appears on the market also as a synthetic—*i.e.*, manufactured product, in a high state of purity. The natural product is obtained as a dense, slightly discoloured powder in huge crystalline areas, and combines the role of flux and semi-opacifier. The role of fluorine as an opacifier is considered under fluorspar. It is virtually indispensable in a white enamel, as it introduces the valuable alumina without hardening the enamel, and in its absence higher percentages of tin oxide are necessary. Its M.P. is 950° C. Up to 15 per cent. in a white enamel is a commercial possibility, beyond which crazing is almost inevitable owing to the high coefficient of expansion. Below 5 per cent. it is useless. Too high a percentage renders an enamel dull, and gives it a poor resistance to acids. Cryolite renders an enamel decidedly soft, and if introduced at the expense of felspar the proportion of quartz should be increased. At about £40 a ton, cryolite is the most expensive ingredient of the frit, and it is for reasons of finance that the presence of quartz as impurity is unwelcome, as it has no deleterious effect. The purest natural cryolite is consumed by the aluminium industry, and it is only poorer grades that reach the enamellers.

True synthetic cryolite (not to be confused with artificial cryolite, which is discussed under sodium silico-fluoride) is of the same composition as the natural product, though it is in a higher state of purity. It is virtually the monopoly of one German manufacturer, and appears on the market as a light fluffy powder containing 98-99 per cent. pure cryolite, the sole impurity being sulphates or chlorides which have not been completely removed; these may easily be tested for as indicated under borax, and this should always be done. If they are absent the material is suitable for use in place of the natural. The synthetic cryolite is made by treating aluminium hydroxide with sodium fluoride, or hydrofluoric acid, etc. The extraordinary difference in the density of the two powders may render necessary changes in the size of the batches. The lightness of the synthetic is an advantage for mixing, but may render the volume of the batch too big for the melting furnace.

Either form is very active in destroying the melting furnace lining.

Cobalt Oxide.—In this compound the two elements cobalt and oxygen appear combined together in varying proportions, and these different compounds have been tabulated according to their cobalt content :—

F F K O,	CoO,	78	per cent.	cobalt.
G K O,	CoO,	76	,,	,,
F K O,	CoO,	75	,,	,,
R K O,	Co_2O_3,	70	,,	,,
S K O,	Co_3O_4,	66	,,	,,
K O H,	$CoCO_3$,	56	,,	,,
P K O,	$Co_3(PO_4)_2$, $8H_2O$,	34	,,	,,
A K O,	$Co_3(AsO_4)_2$, $8H_2O$,	29	,,	,,

The first three are grey cobalt oxide, the first being the specially prepared cobalt oxide of commerce. R K O and S K O are black, the former representing the usual black oxide of cobalt. The metal cobalt was until recent years virtually a chemical curiosity, although its compounds have been employed for colour making in the ceramic arts from time immemorial, and the metal has now achieved importance for a special steel alloy.

The metal itself does not occur in nature, and its ores, in which it is usually associated with arsenic and nickel, are not widely distributed. The principal source is the silver mines surrounding the city of Cobalt in Ontario, Canada, though the ores also occur in Norway and Sweden. The extraction of the cobalt is complicated by its occurrence with iron and nickel, which cobalt strongly resembles in many of its properties, and the separation is, therefore, difficult. The ores are treated by different methods, depending on the nature of the ore and their prospective use, cobalt ores being more often worked to get cobalt salts rather than the metal itself. Those minerals containing sulphur and arsenic are first roasted to remove these ingredients. Iron is partially removed by fusion with limestone, when the metal forms a slag on top of the cobalt and can be removed. The remaining cobalt " speiss " is dissolved in concentrated hydrochloric acid, treated with sulphuretted hydrogen for the removal of copper and associated metals, and then with just sufficient bleaching powder to oxidise the iron, which is then precipitated with milk of lime. To the clear solution more bleaching powder is added to precipitate cobalt oxide, and the nickel remaining in solution is recovered with milk of lime. This lengthy series of operations explains the high cost of the material, the commercial cobalt oxide being priced at 8s. per lb., thus constituting the most expensive of the enameller's raw materials. Should the metal be required, the oxide is treated with either hydrogen or aluminium at a high temperature.

Commercial cobalt oxide always contains traces of iron and nickel, and the detection of these and of the proportions present are duties for an experienced chemist. Cobalt oxide and nickel oxide can readily be distinguished by simply heating a little with borax until fusion results ; cobalt gives a brilliant blue glass, nickel a brown one, but when both metals are present the one masks the other. The presence of cobalt in nickel is usually not of vital importance, but when so-called cobalt oxide is adulterated with nickel oxide the situation is different, since nickel is only one-eighth of the value. Fortunately two chemicals are available which will separate traces of the one metal in the presence of a large quantity of the other. Dimethyl glyoxime when added to a compound of nickel in suitable solution yields a voluminous precipitate of a distinctive pink-red shade, containing about one-fifth its weight of nickel, whilst α-nitroso-

β-naphthol acts similarly with cobalt. A chemical analysis of cobalt will include arsenic and sulphur.

Cobalt first attained importance in the enamelling and glass industry by virtue of the beautiful blue colours obtainable from its use. The original colouring material was a form of smalt, a crude cobalt silicate in a potash glass which continued in use centuries before cobalt was identified. It may be produced artificially by the fusion of cobalt oxide with quartz.

Far more potent combinations of cobalt are now employed, 0·1 per cent. of cobalt oxide giving a distinct blue colour to an enamel, and 1·5 per cent. being the maximum content. Another cobalt mineral used for the same purpose is *zaffre*, the crude cobalt arsenate obtained after the first stage in the ore extraction. Cobalt is a very certain pigment, since its colour is not changed by oxidising or reducing conditions in the furnace. For colour making the prepared grey oxide is preferable, owing to the absence of nickel. Other shades may be produced, such as *Thénard's Blue*, by heating aluminium oxide with cobalt oxide; also *Rinmann's Green*, by replacing the aluminium oxide by zinc oxide.

Cobalt oxide is used in small quantities as an addition to white enamels for neutralising the yellow tint produced by iron. It is further used dissolved in water for branding trade marks, etc., the peculiarity being that the solutions are pink in colour, whilst the dry salts are blue.

The outstanding importance of cobalt in enamelling to-day is in the production of ground coats, which are discussed in Chap. VIII.

The three oxides, CoO, Co_2O_3, and Co_3O_4, all pass into Co_3O_4 on heating, this being the stable oxide. Its M.W. is 241.

Cullet, *see* Ground Glass.

Felspar.—Potash felspar, $K_2Al_2Si_6O_{16}$. M.W. 536. This forms a portion of the felspathic minerals which are widely distributed, other forms of felspar being the soda felspar (*albite*), $Na_2Al_2Si_6O_{16}$, and lime felspar (*anorthite*), $CaAl_2Si_6O_{16}$, which are always closely associated in nature, often in the same crystal, together with *quartz*, *muscovite*, *mica*, *beryl* and *magnetite*. Potash felspar is the only one of interest in enamelling, and is usually available on the market either as a white or pink powder. The presence of the pink colour, which burns out, is often accepted as a guarantee that the felspar is a true potash one, though the colour is easily reproduced. Staley attributed it to the presence of fluorides of iron, FeF_2 and FeF_3, though the latter is not volatile at 1,000° C.* The remaining colour cannot be regarded as quantitative for iron, but depends on the combination, iron silicates being less coloured than the oxide. Only the coarse-grained felspar can be mined commercially, and this from open pits. It shares with borax the distinction of being the material most largely used in enamelling, a position which applies with more emphasis to cast iron than steel, since for the former felspar is often the only source of silica, neither sand, flint, nor quartz being introduced.

The formula is generally written K_2O, Al_2O_3, $6SiO_2$, which indicates better the composition of the material. The theoretical analysis is :—

K_2O, ...	16·9	per cent.
Al_2O_3, ...	18·3	,,
SiO_2, ...	64·8	,,

though in practice the silica is never so low as this. Grünwald advises the rejection of felspar containing above 66 to 68 per cent. silica, though this is nearer a

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* *Roscoe and Schorlemmer*, vol. ii.

minimum than a maximum for felspar available in this country, where 68 to 70 per cent. is the common proportion of silica content.

Felspar is fundamentally a simple enamel in itself, containing the flux, potassium oxide, the refractory, silica, and the necessary stabilising alumina; pure felspar is a flux in the melting furnace, gradually softening at 1,200°. It is available at prices ranging between £4 and £10 per ton, according to quality and method of grinding, wet grinding being more expensive but producing a beautiful material. The ground felspar should all pass 120-mesh, though it is usual for it to pass a 200-mesh sieve. It is preferable to buy it in lumps and grind it at the factory.

The proportion employed in the enamel is intimately connected with the quartz content, and to a lesser extent with the cryolite; the usual practice is 30 to 35 per cent. in both ground and cover coats, though in the latter it may attain 50 per cent. Vielhaber states that more than 22 per cent. of alumina in an enamel produces a dullness, and hence warns against excessive felspar and clay; but as the average content of alumina in enamel is in the neighbourhood of 11 per cent., this allows an appreciable margin. The influence of felspar on the expansion is not altogether favourable, that of the potash and alumina being more than counterbalanced by the low value for silica. Its main virtue consists in the added durability of a felspar enamel, while to a lesser extent some small opacifying effect is also introduced.

Theoretically there should be no loss in weight of felspar during melting, but in practice some of the silica is volatilised with the fluorine.

Though felspars are widely distributed, the best European material originates in Scandinavia. Soda spars are of only subordinate interest, but potassium spar is usually partially substituted with lime spar, which gives very fluid, easily crystallised glasses.

Cornish stone is sometimes mentioned as a substitute for felspar, though it is much harder. Its composition is—

SiO_2,	75 per cent.
K_2O,	5 ,,
Na_2O,	3 ,,
Al_2O_3,	16 ,,

Its name indicates its source. It has no practical use in enamelling, though it is mined for other ceramic industries. Felspar introduces potassium oxide at a cheap rate to enamelling, and this reduces chipping and allows the silica to be readily fusible. Felspar should be bought on a true analysis from bulk, and not on a hand-picked sample. The term potash spar is valueless, being applicable to practically any felspar. The mineral is never deliberately adulterated except with quartz, and this may be distinguished under the microscope. There are plenty of minerals containing only felspar and quartz, and up to 15 per cent. of the latter has little effect on the hardness of the enamels, but since quartz can be bought at prices lower than those of felspar, no one wants to pay first-class felspar prices for such material. Felspar should not effervesce with acid, nor fume with concentrated sulphuric acid.

Where deposits are being worked, constant checking by analysis is necessary, as the composition of the mineral varies suddenly, and the fact that this analysis is insufficiently carried out explains the variability experienced with enamelling felspars. The following pointed comments are made by Staley :—

"Felspar is more variable in composition than any of the other ingredients used in enamels, and the results of these variations are disastrous. Probably more loss has been caused in the enamelling business by variation of felspar than by any other factor.

"When it is realised that few enamellers, and still fewer merchants, know that felspar is sorted into three grades, and that all felspar producers think that No. 3 grade is entirely suitable for enamelling purposes, it is evident that enamellers as a rule get a low grade and variable supply of felspar."

The position in this country is not quite so bad. The equivalent of No. 1 and No. 2 grade spars are supplied to the potteries and good spars are usually obtainable from potters' merchants. In these qualities attempts are made to keep the quartz and iron within low limits, whilst No. 3 is unchecked and contains fines, chippings, and sweepings. The enameller usually adopts the partial safeguard of ordering from the same source, and since he seldom obtains a chemical analysis, he makes a trial batch. Staley advises the further precaution of employing two or more felspars of different composition and blending.

Flint.—*See* Quartz.

Fluorspar.—$Ca . F_2$. M.W. 78. This is the name given to the mineral the chief constituent of which is calcium fluoride. It is mined extensively, occurring in large quantities in Derbyshire, Saxony, and other countries. It appears in all shades from blue to brown, the common name for the mineral in Derbyshire being Blue John. The colour should burn off on ignition, leaving a white powder only slightly discoloured by iron. After screening and rough purification, the composition approximates to 95 to 98 per cent. calcium fluoride, and in this condition the material appears on the market, priced at £4 10s. to £5 a ton.

The chemical composition is :—

Calcium, ...	51·3 per cent.
Fluorine, ...	48·7 „

or more suitably for calculation :—

Calcium oxide, ...	71·8 per cent.
Fluorine, ...	48·7 „

The impurities are silica, chalk, and clay.

It thus introduces into the enamel batch a flux, lime, and an opacifier. Where fluxing is concerned fluorspar plays the same role as calcium carbonate—that is to say, it is difficult to melt (M.P. 1,330° C.)—but when once incorporated it lowers the melting point of the enamel. These opposing features are repeated where acid resistance is concerned, calcium fluoride being an extremely insoluble substance, yet in enamel weakens it against attack. Like limestone, it is more popular in American practice than here, only small proportions, from 2 to 5 per cent. finding employment in white enamel, any repetition of the American figure yielding a dull soapy enamel, but from 5 to 10 per cent. is used in grey enamel as a filling.

Fluorine as an Opacifier.—*True and accessory opacifiers.*

The opacifying power of fluorine has frequently been called into question, but there seems little doubt that this substance either directly or indirectly favourably affects the production of an opaque frit. The difference between a flux made from compounds containing fluorine and one containing none is readily obvious, and a practical test of substituting calcium fluoride and calcium carbonate leads to the same conclusion. How this is brought about is difficult to explain. Fluorine itself is a gas of atomic weight 19, and must consequently be in some form of combination in the enamel frit, unless it is occluded.

It is reasonable to assume that the effect is due to calcium fluoride from fluorspar, and sodium fluoride and aluminium fluoride from cryolite, although in the former case fluorspar must undergo decomposition, since calcium fluoride is difficult to melt, yet it acts as a flux in the enamel (where calcium is probably present as calcium silicate), and in this case fluorine may recombine as aluminium fluoride. The claim has been made that opacity in a frit is due solely to a finely divided alumina and not to fluorine, and though this is extremely doubtful in its entirety, the fact that opacity is due to a fine state of division has much to support it. When the enamel is in the molten state the batch is a homogeneous whole, but on cooling the solution is unable to hold all solids in solution, and the least soluble separate out in a fine state of division. For an explanation as to why this causes opacity it is necessary to consider the case of light passing from one medium to another. It is a well-known phenomenon that if an object is viewed through a thick piece of glass or through water distortion results, and the object appears to be in a position different from its true place. Thus in Fig. 12, if the depth of a river

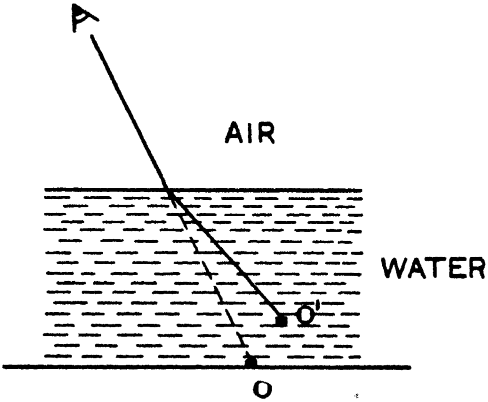

Fig. 12.—Ray of Light passing from Water to Air.

is measured by judging the distance of an object O on the bottom, a low estimate is invariably returned. The reason for this is that a ray of light passing from one medium to another (in this case water to air) is bent from its true course as shown, the object appearing at O′. This effect on the passage of light is said to be due to the difference in the index of refraction of the two materials. In the case of the enamel frit, the two media are the cooled liquid and the finely divided solid which has separated from it, and light passing through the former to the latter is bent. If now this second substance is extremely finely divided, the more particles and consequently the more surface it exposes, and as these lie at all angles, the amount of bending (or refraction) is multiplied, provided the index of refraction differs from the medium to such an extent that the light is completely broken up and distributed in all directions, causing a white opaque effect. This is confirmed by consideration of the true opacifiers, tin oxide, zirconia, and antimony oxide. All these oxides, instead of being opaque, are transparent in their section, but being chemically inactive do not readily combine with other ingredients of the batch, and hence remain in a state of suspension. Furthermore, since they are substances with high indices of refraction, opacity is probably due to refraction of light.

The loss of fluorine during melting is a further matter for controversy. On the one hand, it is asserted that there is no loss; on the other, that all the fluorine is volatilised. Results of analysis indicate that fluorine partially disappears on melting, though the bulk is retained. Grünwald assumes that one-third of the fluorine in cryolite and one-fourth in fluorspar is volatilised (see Chap. VI.), near enough for calculation, though the quantity is dependent on the duration of the melting, amount of silica, and the temperature, slow melting driving off more fluorine. The loss of fluorine takes place in the form of a gas, silicon tetrafluoride, though the loss of silica is negligible. For 1 lb. of cryolite or fluorspar used, there is about $\frac{1}{10}$ lb. silica lost, and as the amount of cryolite and fluorspar used is always limited, the loss of silica seldom exceeds 2 per cent.

Ground Glass or Cullett.—The close relationship existing between enamels and glass has led to this material being introduced into enamel compositions. Without knowledge of the constitution of the glass, it is impossible to say whether or not its inclusion is advisable. The advantages of its use are cheapness, and the fact that, having been melted previously, it is readily incorporated in the enamel batch, but against this is its variability in composition. Apart from special glasses, they may be divided into four classes, the limits of composition of which are :—*

TABLE III.

	Soda-Lime.	Potash-Lime.	Potash-Soda-Lime-Iron.	Potash-Lead.
	Per cent.	Per cent.	Per cent.	Per cent.
SiO_2,	71–78	72–76	60–65	40–50
K_2O,	0–2	12–15	3–5	8–11
Na_2O,	12–17	0–3		...
CaO,	5–15	8–10	18–20	...
PbO,	...	...	...	38–53
Fe_2O_3, Al_2O_3,	1–4	1	6–11	1

Soda-lime glass is a soft glass used for making glass tubes and laboratory apparatus. Potash-lime is a harder glass and more resistant to acids. Potash-soda-lime-iron glass is common or bottle glass, made from the cheapest

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* *Roscoe and Schorlemmer*, vol. ii., p. 572.

materials, and consequently coloured by iron. Potash-lead glass is extremely soft, and used principally for optical instruments. One example of a special glass is "Pyrex," the new cooking ware, which has a remarkable mechanical strength and resistance to change of temperature. Its special feature is a high borax content in a refractory glass, which reduces its expansion to extraordinary low limits, and yet its resistance to water and acids is excellent.

Common cullet is not likely to contain the potash-lead glass, so that for use in a white enamel the chief fear is iron contamination from bottle glass. Cullet is used up to 10 per cent. as a filling, particularly in cast-iron enamels, and coloured enamels generally, sometimes the grinding being omitted and the scrap glass charged in broken fragments. Its value is very small, and its cost will depend entirely on the freightage and grinding.

Iron Chromate, or *Chrome Iron Ore.*—This is somewhat variable in composition, but approximates to $FeCr_2O_4$. It is found in Norway, the Shetlands, United States, etc., and according to Treadwell its composition varies as follows :—

Iron oxide, ...	18–39	per cent.
Magnesium oxide, ...	0–18	,,
Chromium oxide, ...	42–64	,,
Alumina, ...	0–13	,,
Silica, ...	0–11	,,

Its value commercially turns upon its chromium content. In enamelling practice it forms an occasional ingredient of black frits, instead of the iron oxide and chromium being introduced separately. It appears as a dark brown powder, which is simply the ground mineral, and costs about 35s. a cwt. It is used in such small quantities as to have little or no effect upon the physical properties of the enamel.

Iron Oxide.—The term "Iron Oxide" applies to three different combinations of the elements:—

Ferrous oxide,	FeO
Ferric oxide,	Fe_2O_3
Magnetic oxide or black oxide,	Fe_3O_4

The first and third on heating in air pass to the second, which is the important one. This was formerly of interest to the enameller as being the only colouring material available for making red enamels, but it is now used for preparing brown enamels. This iron oxide, which has a chemical composition similar to rust, possesses the property of appearing in almost any shade of purple, red, brown, or black, according to the heat treatment it has received, and it is attention to this particular, in addition to the method of precipitation, which determines the final shade. The iron will probably be obtained from *hœmatite* in either hydrochloric or sulphuric acid solution, and consequently these acids should be well washed out of the resulting oxide and occasional tests made for their presence, as minute quantities will spoil it for use as a colour. Other likely impurities include the soda or lime used for precipitating the oxide.

Iron oxide is used occasionally in the production of frit to be used for making green enamels. For this purpose no nitrate should be included, as the iron is required to be in the ferrous state—that is, as FeO. It imparts a green colour to the fused enamel, the effect of it being seen in bottle green glass or in scraping the white frit which has remained on the furnace bottoms for some time, and becomes thus contaminated with iron.

Black iron oxide, Fe_3O_4, possesses the peculiarity of being magnetic, in which form it is found in nature as lodestone. It is used as an ingredient of black frits.

Ferric oxide, Fe_2O_3, may be used as a colouring material up to 10 per cent. When fritted it has little influence upon the elasticity of the enamel. Its composition is :—

Iron, ...	70 per cent.
Oxygen, ...	30 „

It has a molecular weight of 160, and its cost depends entirely on its purity. It gives a yellow solution with hydrochloric acid, and its presence is always shown by adding a drop of potassium thiocyanate, when a blood-red colour is produced.

Lead.—Compounds of this metal find employment in cast iron enamels, and even here are being steadily replaced. The outstanding advantages are fusibility and high lustre, the drawback, the poisonous nature of lead compounds. Leadless cast iron enamels for domestic ware are now quite common, and whereas the lead was originally replaced by barium, this is now omitted and an enamel similar to that for sheet steel, but softer and higher in borax content, is substituted. Lead is still used extensively for coloured cast iron enamels which are not intended for culinary purposes. Although the user of domestic ware has no cause to fear lead, the question of the use of this material is of wider proportions, for the people making and working the enamels have also to be considered. The Government and other contractors usually prohibit the use of lead and arsenic in enamels applied to iron, and the forbidding by law of the use of these materials altogether in the enamelling industry is well within the realms of possibility during the next few years. The compounds of lead usually employed are lead monoxide, red lead, and white lead. Both lead and the oxides are found native, though the bulk occurs as galena, PbS. Lead is a metal easily melted. The most common process for ore extraction consists in first roasting and then reducing in a blast furnace, where the roasted ore is treated with coke and fluxes, the metal separating from a slag, which takes out many of the impurities, including iron. Freedom from iron is important in glass making. Some metals remain in the lead, rendering it hard, and of these silver is recovered for its own value, but most of the remainder may be oxidised off.

Lead monoxide, PbO, M.W. = 223, occurs in varying shades, the yellow being known as massicot, the deeper shades litharge. This is the stable oxide of lead, and is the starting-out substance for most of the lead compounds, and is largely used in glass making.

Red lead, or *minium*, Pb_3O_4, M.W. 685, is obtained by heating litharge in air to 456° C. Its colour and oxygen content depend upon the care devoted to this treatment; at higher temperatures it passes back to litharge and liberates oxygen, which explains its employment in enamels in preference to PbO. The loss on ignition is 2·3 per cent. Red lead is used largely as a paint pigment, where its value is largely dependent on the high oxygen content.

White lead, $2Pb_3(CO_3)_2$, $Pb(OH)_2$, M.W. 775, was originally made by the Dutch process which consists of subjecting sheet lead to the influence of vinegar vapour together with that of rotting manure or tan bark, a slow process, of from four to five weeks, which has been speeded up by more modern developments. Its most important use is as a white pigment for painting, for which purpose it holds pride of place, as it has a much greater covering power than its substitutes. It is, of course, a poison, and becomes blackened by continual exposure to the sulphuretted hydrogen present in the atmosphere.

For our purpose the " business " part of the above lead compounds is PbO. In the case of white lead it loses 13·5 per cent. by weight on being heated, the loss being carbon dioxide and water, and the resulting substance PbO.

Considering lead oxide as a flux, it fuses readily with silica, and has the effect of appreciably softening an enamel, at the same time producing one of outstanding lustre. Lead oxide also enables more brilliant colours to be obtained than are possible without its use. Its effect on the expansion, etc., of an enamel is not favourable, yet it is considered to give good mechanical properties to the enamel. The quantity of lead which is likely to be dissolved off an article enamelled with its compounds has been considered in conjunction with a Government laboratory examination of the solubility of lead in glazes. For further details, the reader is referred to Thorpe (*Journ. Chem. Soc.*, 1901, lxxix., 791).

Two simple chemical tests for the presence of lead in enamels are (1) boiling the enamelled surface or, better, the powdered enamel with nitric acid (boiling being continued until the nitric acid has been removed), and adding potassium iodide to the clear solution. Yellow crystals of lead iodide indicate the presence of lead ; (2) proceeding as above, but instead of potassium iodide a slightly acid solution of sulphuretted hydrogen is added, blackening indicating lead.

Lime.—*See* Calcium Carbonate.

Magnesium Oxide.—Magnesium is sometimes added to a frit in the form of oxide or carbonate, but it is not to be recommended. This is fully discussed in the next chapter. Like calcium, the batch is difficult to melt, but when melted is very fusible. Having a low expansion, it reduces liability to crazing.

Manganese Dioxide.—MnO_2. M.W. 87.

The only compound of manganese of interest to enamellers is the dioxide, and this finds a use in the preparation of black enamels, and to a lesser extent as a partial substitute for cobalt in grey enamels. Manganese dioxide occurs as the mineral pyrolusite, mainly in the Urals and in India, and the enameller's material is usually the pulverised mineral, though the purer product is the precipitated form, which is to be recommended for exact work. This material bought on an analysis should average 87 to 89 per cent. manganese dioxide, the remainder consisting of lower oxides of manganese, iron, and silica.

The stable oxide is Mn_3O_4, into which MnO_2 passes on ignition, the change representing a loss of 12·3 per cent. ; for simplicity the combining radicle may be taken as MnO. Chemically, manganese resembles iron, and its introduction into enamels is not unfavourable. It may be used up to 10 per cent. for making black enamels, and when these proportions are employed it is as well to divide the amount between the frit and the mill addition. Manganese has a marked effect in darkening the colour of a grey enamel.

Its price is about £24 per ton. The tests for manganese dioxide are that it is soluble in acids, and on boiling up with hydrochloric acid a green solution is obtained and a strong smell of chlorine given. With sulphuric acid oxygen is evolved.

Nickel Oxides.—Two oxides of nickel are of interest :—

Grey NiO contains 75 per cent. nickel (theoretically 78 per cent.)
Black Ni_2O_3 ,, 72–73 per cent. nickel (theoretically 71 per cent.)

The former loses nothing on ignition, the latter 9·6 per cent. Nickel oxides are used almost exclusively as a substitute, complete or partial, for cobalt oxide in ground coats, the substitution effecting a considerable economy ; nickel oxide at 1s. 2d. to 1s. 4d. a lb. is only one-seventh the cost of cobalt oxide. Minerals containing nickel like those of cobalt are found associated with arsenic and sulphur. The ores of cobalt and nickel are found together, and occur in Saxony, Pennsylvania, and Ontario. The treatment of the minerals varies with their nature, though the Canadian ores, containing but 2 to 3 per cent. of nickel, are roasted in the open to oxidise iron and remove some sulphur, next treated in the blast furnace and converted to remove iron and other metals as slag, leaving a matte rich in copper and nickel. The copper is removed by sulphuric acid, and in the Mond process pure nickel is obtained by use of carbon monoxide.

The close chemical association between cobalt, nickel, and iron enables cobalt to be replaced partially by nickel, and the introduction of nickel influences the enamel in exactly the same way as cobalt, though it makes the enamel darker.

Porcelain and Pottery.—Scrap porcelain, which has been reduced to a fine powder, finds employment as a filler for enamels, in a similar manner to cullet, though this material hardens enamels far more than glass. It is safe in so far that blisters will not be caused, since the porcelain has been heated previously to temperatures higher than that of enamelling furnaces.

Though it may be employed in small proportions when the material is known, its indiscriminate use cannot be recommended.

Potassium Carbonate.—Pearl Ash, K_2CO_3, M.W. 138. This is a white, deliquescent powder, used as a flux in enamels in place of sodium carbonate. Potassium carbonate obeys the same conditions as the corresponding sodium compound without material differences, though it produces a harder and more lustrous surface. Its use is not very general owing to the increased expense involved, costing about £24 a ton.

Moreover, 138 parts are equivalent to only 106 parts of sodium carbonate, the loss on ignition to form potassium oxide being 32 per cent. In better class glasses the substitution of the sodium by the potassium compound is of more significance than in our own case.

Potassium carbonate is manufactured in the same manner as sodium carbonate by the Le-Blanc process, the raw material being potassium chloride (which is the main constituent of the Stassfurt deposits) in place of sodium chloride. The ammonia-soda process is not available for the manufacture of potassium compounds.

In common with soda, it increases the expansion, though not quite to the same extent, but reduces the strength and elasticity. It has a melting point of 880° C. The likely impurities are sodium carbonate, chloride, and sulphate.

Potassium Nitrate.—Saltpetre, KNO_3, M.W. 101.

The remarks made above concerning the substitution of potassium for sodium apply again here, potassium nitrate at £28 per ton being about twice as dear as sodium nitrate. In this case there is more justification for the increased expenditure. Potassium nitrate is manufactured from sodium nitrate by treatment with potassium chloride, so that, being a manufactured product, it is likely to be purer. Again, pure potassium nitrate is not deliquescent—*i.e.*, it can be kept dry easily, and further produces a cleaner and a better surface on the enamel.

It is necessary to substitute 101 parts potassium nitrate for 85 of the sodium salt; its impurities are sodium chloride and sulphate; otherwise the notes concerning sodium nitrate apply with equal force to this substance. Its M.P. is 339° C.; 100 parts of potassium nitrate yield 46·5 of potassium oxide on melting.

Pyrolusite.—*See* Manganese Dioxide.

Quartz, Flint, Sand, or **Silica,** SiO_2, M.W. 60.

Silica is the fundamental basis of enamel making, enamels containing 50 per cent. or more silica, though all this amount is not introduced as such, but rather in combination as in felspar, sodium silicofluoride, etc. The three forms of silica mentioned are all minerals and all crystalline, though flint is largely amorphous, being a mixture of quartz and amorphous silica. Other forms of silica are *agate, chalcydony, tridymite, opal,* etc. The two constituents comprising silica—namely, silicon and oxygen—are the two most widely occurring elements in the earth's crust, and in combination occur in all conditions and colours. Quartz possessing a purity of well over 99·5 per cent. may be mined direct, the bulk for the enamelling industry, like felspar, being Scandinavian in origin. The most likely contaminations are iron and aluminium oxides, the former, of course, limiting its use for white enamels, but the latter is not serious if constant.

Much has been written on the substitution of quartz, flint, and sand for one another, and the general conclusion to be drawn is that when these three are present in the same size grain (they should pass 120-mesh) they range in hardness from quartz to sand, the last-named being the hardest, but in practice sand grains are many times the size of the pulverised quartz. Flint is more commonly found in the cast-iron recipes than in enamels for steel, where its inclusion is not generally recommended, though, apart from rendering melting more difficult, it does not materially affect the enamel. The terms are sometimes used indiscriminately. Sand is generally impossible for white enamels owing to the discoloration due to iron, though a beautifully white American sand came to the author's notice which, substituted for quartz in a white formula, produced a harder and more brilliant enamel. This was probably a sample of sand used for glass-making. It is usual to use sand either partially or entirely in place of quartz in ground coats for steel. The best for this purpose is that emanating from Fontainebleau near Paris, and is generally available at about half the price of quartz. A good English sand is mined at Aylesbury, quite suitable for this purpose ; also some Belgian sands are suitable.

The function of these various forms of silica in the enamel needs no description, it being the refractory base, and the enamel is simply a combination between this and the fluxes. Various tables have been drawn up indicating the ratio of raw quartz to felspar which may be safely introduced into an enamel, but the proportions have very wide limits, indicating that the ratio is dependent on other ingredients.

High proportions of raw silica lead to enamels having a low coefficient of expansion, also being very brittle and chipping ; too little causing crazing. Broadly speaking, appreciably more felspar than silica is to be recommended, though when resistance to acids is desired the quartz may be increased. Quartz neither loses nor gains in weight when heated alone, but in the presence of fluorides, which are usually present in enamel batches, a portion is volatilised as silicon tetrafluoride.

Quartz has a melting point of 1,660° C., and is unattacked by all acids except hydrofluoric acid. When heated it undergoes internal changes, passing into other modifications of silica—namely, *tridymite* at 870° C. and *crystobalite* at 1,470° C. Since a change in volume accompanies these transitions, an explanation is afforded of the necessity of heating and cooling silicate bodies gently. Good white quartz is available in pulverised form at from £3 per ton upwards.

Rutile.—This is the mineral from which titanium oxide is obtained. It is an occasional ingredient of an enamel recipe, principally for opacifying purposes, though it is also a refractory. It cannot be employed for the former purpose in the crude state owing to being contaminated with iron (*see* Titanium Oxide, Chap. V., p. 95).

Sand.—*See* Quartz.

Selenium.—Se, A.W. 79. An element of the sulphur family occurring in the mineral condition either as a black or red powder. Its principal service to humanity is due to its peculiarity of having its electrical conductivity affected by light. In enamelling it is employed in conjunction with cadmium sulphide for production of red pigments (see p. 178), and may also be employed as a decoloriser—*i.e.*, compensating for the creaminess due to iron.

Sodium Carbonate, Na_2CO_3, M.W. 106, also known as soda ash or simply soda. Just as quartz typifies the refractory side of an enamel, so soda does the fluxes, and although only 5 to 7 per cent. of this material is added in the raw state, further quantities are present from the nitrate, borax, felspar, cryolite, etc.

Sodium carbonate is manufactured in one of three ways, the raw material being common salt in each case. The original method was that due to Le Blanc, and consisted in first treating salt with sulphuric acid to produce sodium sulphate, then heating this with coke and limestone, when sodium carbonate associated with many impurities is obtained. This product, on account of its colour, is known as black ash, the principal impurity being calcium sulphide, and the final stage in the manufacture consists in washing out the soda and crystallising. This outline of the method indicates the likely impurities, potassium salts associated with the original rock salt, chlorides, sulphides, calcium compounds and caustic soda.

A purer product is now manufactured by the Solvay process, also known as the ammonia-soda process, owing to the use of ammonia as a reagent. In enamelling recipes ammonia-soda is often shown as though it is a distinct compound, but it simply means soda obtained by this process, and this contains no ammonia, the term being used to indicate that a pure soda is required.

In the process brine is pumped direct to the carbonating tower, where it is treated with carbon dioxide and ammonia under carefully regulated conditions. Sodium bicarbonate is deposited from the solution, and is collected, dried and ignited, yielding soda ash. The only likely impurity is sodium chloride.

A smaller quantity is produced by the electrolytic method of treating salt. Here the primary object is to produce caustic soda, and generally it would not pay to carbonate this to produce sodium carbonate, but under special circumstances this manufacture is carried on.

Sodium carbonate as supplied to the enameller is a fluffy powder of purity exceeding 99·5 per cent. On heating, about 41·9 per cent. by weight is lost as carbon dioxide. Its composition is :—

Na_2O, ...	58·1 per cent.
CO_2, ...	41·9 „

It is available in bulk at £6 to £7 a ton, according to quantity.

Washing soda is occasionally recommended as a cheaper substance to employ, especially for the pickling department, but it is usually false economy. When pure this has the composition $Na_2CO_3, 10H_2O$, or

Na_2O, ...	21·6 per cent.
CO_2, ...	15·4 „
Water, ...	63·0 „
	100·0 „

It is thus seen that nearly three times as much of this substance is necessary to produce the same quantity of sodium oxide in the melt, in addition to which there is the heat required to drive off the high percentage of water as steam. Washing soda is usually the crude material, and not of equal purity to commercial soda ash, M.P. 852° C. It gives a clear solution in water when pure, and its strength may be determined by titrating against standard acid. It should give no precipitate with silver nitrate in the presence of nitric acid. Soda, when used to excess in enamels, produces lustrous enamels which are very weak in their resistance to acids or even water, the latter causing them to become dull owing to absorption. Having a high expansion, soda imparts this quality to an enamel, together with elasticity, but renders the enamel mechanically weak. Its further service to the enameller is that it is used as a neutraliser after pickling with acid, and as a mill addition for grey enamels, which is commented upon elsewhere.

Sodium Nitrate.—$NaNO_3$, M.W. 85. Also called Chili saltpetre. This substance is introduced into enamels purely because of its oxidising action. That is to say, it gives off its oxygen readily at low temperatures, and consequently neutralises the reducing action of the fuel. This is necessary in order to minimise the colour effect of the iron, which, as pointed out elsewhere, is far more potent when unoxidised. The composition of sodium nitrate may be expressed :—

Na_2O, ...	36·5 per cent.
N_2O_5, ...	63·5 ,,

The percentage of N_2O_5 is lost in the melter as gaseous oxides of nitrogen, and oxygen. The sodium oxide simply joins forces with that obtained from soda, cryolite, etc. Sodium nitrate is mined as the name implies in huge quantities in Chili, where it is known as *caliche*, and is associated with salt, sodium sulphate, iodate, chlorate, and perchlorate. Purification consists of solution and crystallisation, after which it is graded. The refined quality which is that used by enamellers contains about 97·5 per cent. sodium nitrate, and less than 0·5 per cent. muriates (*i.e.*, chlorides) is usually guaranteed. The material is invariably discoloured by iron, often being a dirty brown in colour.

The impurities are readily discovered by treatment with water and an examination of the residue. All the sodium nitrate dissolves, and the presence of chloride and sulphate may then be tested for as usual. A more modern preparation of sodium nitrate largely developed during the war, owing to inability to procure Chili saltpetre, is that of utilising the nitrogen of the air. This is made to combine with atmospheric oxygen merely by passing air quickly between two highly charged electrodes. A temperature exceeding 2,000° C. must be obtained and quickly dissipated, to prevent decomposition of the nitric oxide obtained. The products of combustion are dissolved in water and alkali, and sodium nitrate thus obtained. This material is beautifully white and pure, but exceeds the natural in price.

Sodium nitrate melts at 317° C., and hence is one of the most active fluxes. Its cost varies with the season and demand for it as a fertiliser, ranging from £13 to £15 a ton. It is thus much more expensive than soda, and the proportion used should be minimised. This need not exceed 3 per cent., in which case the iron impurity is immaterial. Higher proportions are necessary when lead and antimony are used owing to these being reduced to metals, whilst a case has been reported of nickel in ground coats being reduced to the metal and sinking to the bottom of the bath.

Sodium Silico-fluoride, Na_2SiF_6, M.W. 188. Also known as sodium fluosilicate, artificial cryolite, and cryolite substitute. Artificial cryolite is a misnomer for this material, the constituents being entirely different, this latter containing no aluminium and cryolite no silica, the compositions being compared thus :—

	Cryolite.			Sodium Silico-fluoride.	
	NaF,	60 per cent.		NaF,	44·7 per cent.
	AlF_3,	40 ,,		SiF_4,	55·3 ,,
or	Na_2O,	44·3 ,,	or	Na_2O,	33·0 ,,
	Al_2O_3,	24·3 ,,		SiO_2,	31·9 ,,
	F_2,	54·3 ,,		F_2,	60·6 ,,

Sodium silico-fluoride, though known and used before, came into prominence during the war, when freightage of cryolite was restricted. It is a by-product from superphosphate works, the raw materials for this purpose being *apatite* and *fluorapatite*—that is, calcium phosphate containing calcium fluoride. This on treatment with sulphuric acid forms superphosphate of lime and frees hydrofluoric acid, which on coming into contact with silica produces fluosilicic acid, which on neutralising with soda produces sodium silico-fluoride. It is sometimes thrown out of solution with salt, which is, therefore, a possible impurity. In its pure form it appears as a light, fluffy powder having an irritating effect on the eyes and nose. All samples which have come under the author's notice have been of a high state of purity, for testing which Grünwald gives a simple and expeditious method in "Theory and Practice of Enamelling," p. 10, the procedure being simply to treat a known weight with caustic soda of known strength, using phenolphthalein as indicator of end point. The success of this depends on there being no extraneous alkaline or acid salt present. That these artificial cryolites are sometimes crudely adulterated may be gathered from Grünwald.

Sodium silico-fluoride when introduced into enamels acts as an active flux in a similar manner to cryolite, and although claims are made for its efficiency in opacifying, the author has never been able to confirm this, either when substitution is made weight for weight, or by total readjustment of the formula to produce the same final compound as indicated in Chap. VI., p. 110. Weight for weight substitution is doomed to failure owing to the appreciable increase in silica with consequent reduction in alumina. To balance this, it is necessary to omit raw quartz entirely and increase felspar unduly, or have a high percentage of clay. The cost of sodium silico-fluoride fluctuates appreciably, recent quotations being between £14 and £22 a ton, and the opinion has been expressed that it becomes a commercial proposition when the price falls below half that of cryolite. After many indulgent trials, the conclusion to which the writer was drawn was that to produce the greatest opacity per £1 spent, the maximum inclusion of cryolite was to be employed to the exclusion of substitutes.

Whiting, *see* Calcium carbonate.

Witherite, *see* Barium carbonate.

Zinc Oxide, ZnO, M.W. 81.

Zinc oxide is now rarely seen as a constituent of steel enamels, though it is still retained in many cast-iron formulæ, where it is employed both as a frit ingredient and as a mill addition. Zinc occurs chiefly as zinc blende, the sulphide ZnS, though it also occurs in nature as the oxide and carbonate. The extraction of the metal comprises a distillation process, when if the vapour is allowed to come into contact with the air, the oxide is produced. Zinc oxide is the commercial zinc white, used largely for paint-making, which industry claims the better qualities, the "Red Seal" grade being that supplied to the enameller. This is usually somewhat creamy in colour and available at 35s. a cwt. At the temperature of the melting furnace there is no loss on ignition, though at 1,400° it vaporises. In the melt it acts as an active flux, and helps to yield a thin, mobile melt, in which the presence of zinc can be detected by the yellow tinge given to it. Zinc oxide shares with titanium oxide, and to a lesser extent antimony oxide and tin oxide, the ability to appear yellow hot and white when cold. Zinc oxide, though readily soluble in acids, is claimed to be more resistant to acid attack when fritted than the alkali compounds, hence it is usually a constituent of acid-resisting enamels. It has a low expansion, but a high elasticity. Zinc oxide is sometimes retained in coloured enamel, owing to its affecting pigments and producing new shades. Claims are also made for its opacifying effect owing to the production of zinc spinel in the enamel. The simplest test for zinc oxide is the ignition of a little with a trace of a solution of a cobalt salt ; a green mass is obtained. The oxide should not effervesce with acid.

CHAPTER IV.

THE RAW MATERIALS (*Continued*).

Clay and Other Mill Additions.

THE substances added to the frit when about to be ground to make the liquid enamel include a medium for holding the enamel in suspension, and the tin oxide or its substitutes (which are dealt with in the next chapter) in the case of white enamels, and the prepared coloured oxides in the case of coloured enamels.

The substance employed for suspending the enamel is clay, this being the cheapest available material, in addition to which it is composed of ingredients which are common to enamelling. Pure clay is an aluminium silicate possessing the formula Al_2O_3, $2SiO_2$, $2H_2O$, the molecular weight being 258. The formula corresponds to :—

Al_2O_3,	39·6	per cent.
SiO_2,	46·5	„
H_2O,	13·9	„
	100·0	„

—but in practice this composition is never attained, and many of the clays found in nature differ widely from this constitution. Clays are classified into China clay, plastic clays, fireclay, ganister, loam, loess, marl, etc., according to their composition and qualities. The only ones of interest in enamelling are the ball and pipe clays, which are highly plastic, and China clay, which was considered in the previous chapter, and is seldom used for floating enamels, as it is insufficiently plastic. The term pipe clay applies to all whitish clays, and, of course, a clay which burns white is essential for white enamels, though for coloured enamels, cheaper and often more plastic clays exist, a high content of iron oxide preventing their use for white enamels, but being no handicap for other purposes. The power of plasticity is the ability to absorb and hold liquid in the pores of the clay, forming a mass that can be kneaded, and shaped, which shape after uniform shrinkage it retains on drying. This property, of course, is essential to the potter, and in a different connection to the enameller, for the plastic clays are the best for forming suspensions in water. The property of plasticity is not peculiar to clay, but is highly developed therein. Up to 35 per cent. of its weight of water may be necessary for the maximum development of plasticity. Many explanations exist as to the cause of plasticity, including :—

(*a*) The very small size of the grains of clay, the maximum diameter of which is stated to be 0·005 mms.

(*b*) The interlocking grain theory, which assumes the existence of interlocking plates of clay and *kaolinite* (a crystalline substance of the same composition as pure clay). This also depends on grain size, the finer particles being more plastic, and the property is measured by the tensile strength of the sample.

(*c*) The plate theory, which depends on the existence of small transparent plates bunched together.

(*d*) The most popular explanation, which includes most of the above, and agrees most nearly with modern scientific conceptions, is the colloidal theory.

Many substances when reduced to a very fine state of division can be held in suspension in a liquid medium in which they are not soluble, and yet any attempt to separate the solid from the liquid by decantation or passing through a filter paper fails. Most solids take on new properties when so divided, as, for example, many of the metals when reduced to the colloidal state yield a dirty-looking liquid by reflected light, but exhibit beautiful colours by transmitted light. The well-known pigment, "Purple of Cassius," is considered to be a colloidal solution of gold with tin oxide, and is made by the addition of a dilute solution of a tin salt to a similar one of gold, possibly in the presence of salts of other metals. The final product contains about 30 per cent. of gold, and is considered under the enamelling pigments in Chapter IX. Further examples of colloidal solutions include tea, starch, gum, and the gelatinous iron, aluminium, and chromium hydroxides obtained by adding ammonia to solutions of these metals. The jewel opal contains nothing else but silica, but its peculiar beauty is attributed to the silica being present as a colloid. A simple example of colloid formation, which is the most usually quoted, is the case of sodium silicate (water glass) and hydrochloric acid. When concentrated acid is added to the water glass, a white precipitate of hydrated silica is produced, which on standing settles to the bottom of the vessel, and may be separated and collected on a filter paper in the usual way. Common salt, which is formed at the same time, passes through in solution. If, however, dilute acid is added gradually to the water glass, the liquid turns opaque, but no such separation is now possible. The silica is now in the colloidal form, and to separate it from the salt it is necessary to pass it through a parchment membrane, when the salt again passes through and the silica is retained. In distinction from the colloid, salt is said to be a crystalloid. Since in these two examples silica was in the one case colloidal, and in the other non-colloidal, existence as a colloid is a state, and not a property, of certain materials. A colloidal solution on prolonged standing generally settles out, when it may be treated as an ordinary suspension; thus clay in water will eventually precipitate itself. Further examples of colloidal solutions and their deposition include the case of river sludge being carried down to the sea. The suspension here is colloidal in nature, but when it meets the salt water at the river estuary it becomes deposited, thus forming the deltas common in river mouths. When sulphuretted hydrogen gas is passed through a solution of arsenic acid a fine yellow colloidal solution of arsenic sulphide is produced, but on the addition of hydrochloric acid or certain salts the precipitate coagulates. A similar phenomenon exists in the flocculation of clays, suspended in water. The particles of clay are of the dimension of 0·1 mm. for the coarse grains and less than 0·01 for the fine, some being too small to be seen even under a high power microscope. These form a colloidal solution in water, and the addition of substances dissolved in water, commonly known as "salts," may influence these to the extent of causing the clay particles to settle to the bottom as a precipitate. The study of the theory underlying this action is in the realm of advanced chemistry, and quite beyond the scope of this work, and, further, is still the subject of controversy, but a superficial acquaintance with it is helpful in deciding the action certain salts will have on a clay suspension.

Any salt dissolved in water is considered under the ionic theory to partially dissociate into its integral parts, as, for instance, common salt (NaCl) into sodium and chlorine ions, and these, besides being capable of conducting an electric current, are supposed to be charged electrically themselves, the charge on the sodium ion being opposite to that on the chlorine ion, the salt in solution being known as an electrolyte. Furthermore, colloidal solutions are also considered to be charged electrically, hydrated alumina being positive, and hydrated silica negative, and the coagulation of these is due to the reduction or removal of the charge upon them, either by the direct method of applying an electric current to them, or by the addition of the previously mentioned electrolyte.

In the general investigation of colloids, calcium and magnesium salts have been found to be more effective in coagulating negatively charged particles than potassium or sodium, and aluminium is still more effective than any of these. Similarly a sulphate is more effective than a chloride, bromide, or nitrate for coagulating positively charged particles. This explains why Epsom salts (magnesium sulphate) is one of the most effective "salts" known for this purpose. A further reason is because this substance on coming into contact with the alkali of the enamel decomposes with the production of a precipitate of magnesium hydroxide, which also helps in suspending the enamel, another salt, sodium sulphate, being left in solution, thus :—

$$\begin{array}{ccccccc} \mathrm{MgSO_4} & + & \mathrm{2NaOH} & \rightarrow & \mathrm{Na_2SO_4} & + & \mathrm{Mg(OH)_2} \\ \text{Magnesium} & & \text{Sodium} & & \text{Sodium} & & \text{Magnesium} \\ \text{sulphate} & & \text{hydroxide} & & \text{sulphate} & & \text{hydroxide.} \end{array}$$

That this neutralisation of electric charge is far from being a complete explanation of the coagulation of colloids is indicated by the fact that the result can be achieved with insoluble materials (*i.e.*, non-electrolytes). In the consideration of colloidal solution, theory lags behind practice, and where clays are concerned, the position is very complicated, because the conditions vary in each specific case; the composition is variable, and in addition to the salts to be added the enamel frit is also present, which yields an alkaline solution, and this either acts with or against the salt addition, the degree to which it is effective depending on the frit. In this connection it is sometimes observed that it is impossible to stiffen an enamel by any of the usual salts, and this applies particularly to enamels rich in cobalt oxide or chromium oxide. Occasionally the addition of acid will flocculate the clay, though usually the reverse is the case. The most potent salt additions usually adversely affect the finished enamel, and consequently the enameller has to temper efficiency with a consideration of other desired qualities.

During the first additions of salt the coagulation is proportional to the amount added, but after a time no further coagulation results, and then the reverse effect sets in. The salts employed may be placed into three classifications, (*a*) salts made from a strong base (metal) and weak acids—*i.e.*, positive in action; (*b*) strong salts—that is, from a strong base and strong acid; and (*c*) salts from weak bases and strong acids, and negative in action. Examples are:—

A.	B.	C.
Borax.	Sodium chloride.	Ammonium chloride.
Sodium carbonate.	Sodium sulphate.	Magnesium chloride.
Ammonium carbonate.	Potassium sulphate.	Magnesium sulphate.
	Potassium chloride.	Alum.

The relative value of these is discussed later.

There is more variation in the composition of clays than any other enamelling material, largely because it is a mineral which is very widely distributed and closely associated with other rocks, and because it is a material which is difficult to examine thoroughly, and goes through little in the way of refinement. There is some protection in buying lump clay, because dirt is then more readily visible, and little extra labour is incurred, because the lumps easily disintegrate in water. Reputable merchants supply clay to enamellers in pulverised form, washed and dried, which is a perfectly safe material to handle.

Undoubtedly the best treatment is to boil the clay at the enamel works. All that is required is a series of tubs placed on a flue, the tubs holding either a mill full, or half a mill of water, into which the necessary amount of clay is weighed. After boiling, all the true clay substance can be drawn off with the water and the dirt and other impurities will be left in the tub. Bacteria are always present in clay suspensions, some of which are gas producing, and which if left in may cause pinholes in the enamel, but the boiling destroys them.

Clays are produced by the weathering of other minerals of felspathic nature—that is, the continued action, through the ages, of rain and atmosphere. Grünwald gives an equation representing such natural decomposition of felspar.

$$\underset{\text{Felspar}}{K_2Al_2Si_6O_{16}} + \underset{\substack{\text{Carbon}\\\text{dioxide}}}{CO_2} + \underset{\text{Water}}{2H_2O} \rightarrow \underset{\text{Clay}}{Al_2O_3, 2SiO_2, 2H_2O} + \underset{\substack{\text{Potassium}\\\text{carbonate}}}{K_2CO_3} + \underset{\text{Silica.}}{4SiO_2}$$

The silica is deposited as sand, whilst the soluble potassium carbonate is washed away together with the fine clay particles, these latter being deposited at later stages of the water's course, where they are a secondary deposit in distinction from primary clays, which are deposited at the original point of weathering. The world's crust is largely composed of *granite* and *gneiss*, which are rich in felspar, and the likely impurities in clay are, therefore, quartz, mica, potassium and sodium salts, organic matter, and *zeolites*. Together with weathering, but distinct from it, another form of decomposition proceeds with the production of *kaolinite*, and is known as "kaolinisation." The *zeolites* are the alkaline salts of alumino-silicic acid, and are now made artificially in appreciable quantities for use as water softeners.

On heating to 450°–500° C., clays lose their water content and plasticity, and at higher temperatures (1,470° C.) crystals of *sillimanite* appear. This material is now being used as a refractory, and is discussed in Chapter X. It is present to the extent of 3 to 5 per cent. in plastic clays, and 20 per cent. to 25 per cent. in china clay.

That the English pipe and ball clays occurring in Dorset and Devon are of very high quality is indicated by their being exported to America, but the best enamelling clays are to be found at Vallendar near Coblenz on the Rhine, Germany. These are more plastic and more constant in composition than the average clay. The composition of some clays is appended :—

TABLE IV.

	Grünwald.	American Plastic.	Vallendar.	General Limits.
	Per cent.	Per cent.	Per cent.	Per cent.
Al_2O_3, . . .	31·34	19·9	32·1	11–40
SiO_2, ...	51·55	68·5	56·7	40–60
Fe_2O_3, ...	Less than 1 per cent.	0·8	Traces	2
CaO and MgO, .	Nil	Traces	Traces	0·5
H_2O, ...	...	...	3·8	5–14
Na_2O, ...	...	0·2	...	0·5–1
K_2O, ...	...	1·6	...	...
TiO_2, ...	...	1·2	...	...
Loss on ignition (inc. water).	...	7·8	6·7	...

When buying clay, it is advisable to specify "air-dry," otherwise it may be associated with an indefinite quantity of water, sometimes to the extent of rendering the whole mass pasty. This buying of unnecessary water is aggravated when purchasing from the Continent, as the freightage represents about half the bill. The best quality white clay should be available at prices below £7 per ton.

The examination given to a clay usually begins and ends with rubbing a moist finger on a piece to feel the soapiness, though a simple and useful test is to measure its softening ("melting") temperature, a test which indicates at the same time whether it is a white burning clay. Treating with acid will indicate the presence or not of chalk, as in the affirmative effervescence will result.

The more thorough examination of clay is a difficult matter. Analyses are of two types, ultimate analysis, which means a complete examination, or rational analysis, which is a simpler procedure on a rule-of-thumb basis. The complete analysis of clay is a long and tedious business, and most of the published analyses are worthless, since they either indicate no figures for the alkali metals or else show determined figures for the other ingredients, and the alkali metals are shown by difference from 100 per cent. This is a worthless result, since 0·1 per cent. of an alkali influences the clay tremendously. The exact determination of the various ingredients in clay is useful in indicating its source and likely suitability for its projected use. The radicles looked for and their effects are, in addition to alumina :—

Silica.—Silica in clay is an anti-shrinking agent, a property which increases its value to the potter, and which increases with grain size. It increases the refractoriness only in clays high in fluxes, since its effect on a high aluminous clay is to reduce the melting point, as indicated in Chapter II., p. 27. A high percentage of silica indicates a sandy clay.

Iron Oxide.—The principal effect of iron oxide is to colour the clay, though at high temperatures (above enamelling) it acts as a flux. Up to 32 per cent. iron oxide may be found in a brick clay.

Lime and Magnesia.—These act as fluxes, but are objectionable in the finished enamel. Magnesia is distinct from lime in that it does not vitrify suddenly and does not affect the colour of iron, which is turned buff by lime. A high lime content indicates the calcareous nature of the clay.

The Alkalies (K_2O and Na_2O).—These remain in the clay from the original felspar. They act as fluxes, and are desirable except in refractory clays. Usually present from traces up to 1 per cent.

Titanium Oxide, TiO_2.—This is present in most clays, and though under ordinary circumstances would be regarded as a refractory, its effect on clays is to lower the melting point.

Organic Matter.—This is the portion which burns off at 800° to 900° C. It may be vegetable or bituminous in nature, and is an important ingredient. The smell of clays has been attributed to this portion, and it is also considered to influence the colloidal matter.

The Loss on Ignition includes the above organic matter and the water of constitution.

Soluble Salts.—This is the portion soluble in water, and consists of such salts as calcium sulphate, iron sulphate, sodium sulphate, and potassium sulphate, all of which are objectionable.

Rational Analyses.—Various schemes of rational analysis have been drawn up, and owing to their simplicity have achieved some prominence, most of them comprising the treatment of clay simply with acid and alkali of definite strength, and weighing the amounts extracted, then by calculation figures are obtained representing the proportion of :—

True clay substance.
Quartz.
Felspar.
Mica.

This rough and ready examination may be of some small value for comparative purposes where the different clays are treated under the same conditions by the same worker, but the worth of their conclusions has been very strongly questioned. A scheme is here appended to indicate the procedure :—

Two grammes of the material are treated with 20 c.c. dilute sulphuric acid, and the excess acid removed; 1 c.c. concentrated hydrochloric acid and boiling water are then added. The insoluble matter is filtered off and digested with 15 c.c. boiling 10 per cent. caustic soda; 25 c.c. water are added, and liquid filtered through the same paper. The residue is washed five or six times with boiling water. The residue is now treated in the same way with hydrochloric acid, dried, ignited, and weighed. The alumina found insoluble in sulphuric acid and caustic soda is multiplied by 3·51, this factor representing the average ratio of SiO_2 to Al_2O_3 in *orthoclase felspar*, hence the product represents silica in undecomposed felspar. The sum of this silica with alumina, iron oxide, and alkalies equals "felspathic detritus." The difference between silica as calculated from felspar and total silica in the insoluble portion represents quartz. The difference between portion of sample insoluble in sulphuric acid and caustic soda and the total 2 grammes equals clay substance.

Felspar renders the clay easily fusible, but has little plasticity. Kaolinite is plastic, refractory, and shrinks considerably. Mica, if extremely finely divided, is a flux ; if not finely divided it is a refractory. Below 1 or 2 per cent. may be neglected. Quartz is non-plastic, and has a low tensile strength.

The conclusions obtained from either analysis are incomplete from the enameller's point of view, and a

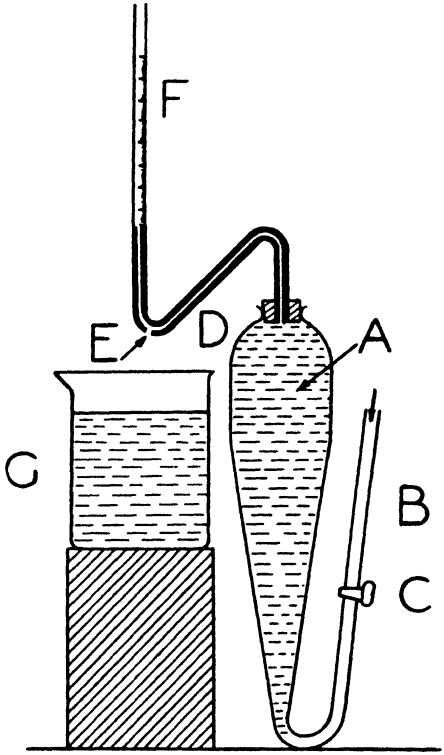

Fig. 13.—Schoene's Elutriator.

far more useful examination is by means of the apparatus illustrated in Fig. 13. It is known as **Schoene's Elutriator,** and this, or a more modern adaptation of it, is used primarily for measuring the size of particles. It can be used for washing out and measuring the true clay substance in a commercial clay. In principle it consists of the glass vessel A of standard dimensions, into which a known weight of clay is placed, and which is fed through the tube B with a constant supply of water, capable of regulation by the tap C. Through the rubber cork D, an S-shaped barometer tube (*i.e.*, thick walls and narrow bore) is inserted, having a round aperture of definite dimension at the point E. Above this is fixed the vertical tube F, graduated in centimetres. After the instrument has been standardised it is possible, by gradually raising the height of water in F by stages, to separate the clay particles from the smallest to the largest, since the greater the flow of water, the heavier the particles which can be lifted from the clay and carried through the hole E to the container G. After such increase in pressure the extract can be weighed and the size of particle calculated, the impurities in the clay being left behind in the vessel A. It is usual to work on air-dry clay which has been passed through a fine sieve to remove extraneous matter. About a gallon of water is required for each separation.

Action of Clay in Enamels.—Since clays form about 6 per cent. of the final enamel, they appreciably affect the chemical and physical qualities of it, in addition to their primary role of floating the enamel. It is conceivable that the first 2 or 3 per cent. of clay may lower the melting point of the enamel, but beyond this, an increase of clay gives a higher melting point, and the figure has been stated at 50° C. for every 1 per cent. The average addition is in the neighbourhood of 7 per cent. of the frit used, of which about one-seventh burns away as moisture. The proportion of clay may be varied during the summer and winter months by about $\frac{1}{2}$ per cent., since during the summer, when drying is quicker, so much clay is not necessary. An excess of clay gives a dull, lustreless enamel, hence clays of poor plasticity requiring a bigger proportion are to be avoided.

The cost of the best clay is so low compared with the rest of the enamel, and it occupies such a comparatively appreciable portion of the finished enamel, that any price cutting in clay is usually false economy. Clay has an opacifying value and favourably affects the elasticity, expansion, and tenacity of the enamel, at the same time rendering it more resistant to sudden temperature change.

The fault known as water-marking (that is, a zig-zag line forming) is intimately connected with the clay, and is produced when large enamelled areas are dried too quickly, this causing the clay to shrink too quickly, with consequent fracture. A similar result is obtained when drying is too slow, when clays of poor plasticity part, and fail to hold the enamel together. Apart from a more reasonable method of drying, the best cure is a slight increase in the clay content, or giving the article a light dusting with dry, fine ground enamel through a sieve immediately after dipping. The fault occurs on flat work, and in the insides of tall articles such as jugs and pails, which are slow to dry. After an enamel has set, the tiniest drop of water applied at the top will pursue a zig-zag course down the article to the bottom, breaking the biscuit along its path.

Bentonite.—These remarks on clay would be incomplete without reference to the interesting material *bentonite*, which possesses a much greater suspending power than clay, it being in fact five or six times as effective. Bentonite is a little-known mineral occurring to a limited extent in Canada and the U.S.A., the centre of the industry being Wyoming. It is employed as a filler for paper, textiles, rubber, and soap (though it is claimed to have cleansing properties in this latter case, and not merely to act as a filler). Serviceable enamels have been produced using only 1 or 1¼ per cent. of it in place of clay, but this renders the enamels so short that they are somewhat difficult to work, and produce a wavy effect. Further, if a batch is accidentally made thin, it is impossible to thicken it with the aid of salts. The suspension with bentonite remains indefinitely, no settling taking place, as is the case with clay. Naturally, if adopted, the frit needs some reconstruction, as the enamel is appreciably softer, using a much softer clay, and a smaller proportion of it. In appearance, the material is a waxy powder, slightly tinted and burning somewhat cream. It may be distinguished from clay by either fusing in a blowpipe, when the edges soften, or by dropping into water, when the particles swell and assume the consistency of soft soap. The analysis is given as :—

SiO_2, ...	59·8–69·5	per cent.
Al_2O_3.	11·8–26·6	,,
Fe_2O_3, ...	2·5– 3·3	,,
CaO, ...	2·9	,,
MgO, ...	0·2– 2·76	,,
K_2O, Na_2O, ...	5·5–13·8	,,

The high alkali content explains its softness and possibly the high plasticity.

The study of clays is such a wide subject that only the merest outline has been given here: The literature on the subject is extensive, and any reader desiring further information is referred to "Clays, Their Occurrence and Use," Ries, or the numerous works of A. B. Searle. The Elutriator is described in Wiley's "Principles of Agricultural Analysis," vol. ii.

The salts most commonly used for flocculating clays are :—

Alum.—Aluminium potassium sulphate, $Al_2(SO_4)_3$, K_2SO_4, $24H_2O$, M.W. 948. A very strong salt for the purpose, but not to be recommended. If completely burnt off it yields potassium and aluminium oxides, but this result is not achieved in the fusing furnace, some sulphate remaining to spoil the enamel. Beautiful crystals of this material may be obtained by adding a solution of aluminium sulphate to potassium sulphate in the requisite proportion and allowing to stand. It is manufactured from china clay by treatment with sulphuric acid.

Ammonium Carbonate.—A salt of indefinite composition. Though not the most potent of flocculating agents, it is extremely useful in that it leaves no residue on heating. It is obtained as white crystals by heating a mixture of chalk and ammonium chloride, when the ammonium carbonate sublimes away and crystallises on a cold surface; it is also known as *sal volatile.* It costs about 5d. per lb., and is thoroughly recommended as the most harmless of these necessary salt additions.

Ammonium Chloride, NH_4Cl, M.W. 53·5.—Also known as *sal ammoniac.* This substance is obtained from ammonium sulphate by treatment with salt. All ammonium compounds have their origin in the ammoniacal liquor, which is obtained when coal is distilled in gas works. The ammonia so obtained is bubbled into sulphuric acid, forming ammonium sulphate, the starting-out material for all these compounds. Ammonium chloride is a strong salt, but is again objectionable. Theoretically, ammonium chloride is volatile, and, as this happens partially, the salt is less unwelcome than magnesium chloride, but nevertheless some chloride remains in the enamel, and the general acid character of the substance is foreign to enamels.

Borax, $Na_2B_4O_7$, $10H_2O$.—Finds employment for ground coats only, and in this respect is discussed in Chapter VIII. Its rapid decrease in solubility in water with falling temperature renders it imperative that the enamel be maintained at a reasonable temperature. No other salt is necessary for ground coats excepting a small quantity of soda where rust marks occur.

Magnesium Carbonate and Oxide.—These two substances have an identical effect upon the enamel, the former passing into the latter on ignition. Both are available in light and heavy form, the light being generally recommended. It appears as a light fluffy powder, and may be distinguished from the carbonate by the latter giving an effervescence when treated with acid. The oxide is generally known as "calcined," and costs about £4 10s. per cwt., against £2 2s. for the carbonate, but there is no economy in the latter, since 2·1 times as much are necessary to produce the same effect. The composition of magnesium carbonate is :—

MgO,	47·6	per cent.
CO_2,	52·4	,,
	100·0	,,

Magnesium carbonate is found native or is manufactured from limestone by treatment with magnesium chloride, the oxide being obtained by the ignition of the carbonate. Both materials sold to enamellers are in a high state of purity. Neither is very soluble in water, and these two substances afford an example of the case mentioned of insoluble substances flocculating clays. They are as near harmless as any salt addition can be, and when these are necessary in a white or coloured enamel, about 1 oz. of the oxide to 100 lbs. of frit is a suitable addition.

Magnesium Chloride, $MgCl_2, 6H_2O$, M.W. 203.—Magnesium chloride is found native, and in association with other chlorides. The white crystals are very deliquescent, and consequently always moist. As an addition to clay it is very strong, but not to be recommended.

Magnesium Sulphate (Epsom salts), $MgSO_4, 7H_2O$.—As the name implies, this substance is found native in the neighbourhood of Epsom. A white, crystalline substance, it is the most potent salt employed, and retained by nearly every enameller as a stand-by. When regarded as a medicine only to be applied in minute quantities when the case is sufficiently serious, it is a valuable asset. Its services, however, are too often abused. The cost is 3d. to 6d. a lb.

Potassium Carbonate and **Chloride, Sodium Carbonate** and **Chloride.**—Apart from the small service sodium carbonate may render to ground coat enamels, as mentioned under "borax" above, none of these substances serves any useful purpose.

Sodium Silicate (water glass).—This substance may occasionally be found to serve a useful purpose, though it is extremely difficult to judge the correct amount to use. Even in very dilute solution, and added with all due caution, as each succeeding drop is added no apparent effect is produced, until all of a sudden a severe thickening takes place, and a few minutes later the whole mass may jellify. Sodium silicate has the virtue of producing a very firm biscuit enamel.

Summing up, the author follows Grünwald in considering that all salts are to be avoided except when absolutely necessary. Where employed, borax should completely meet the case of ground coat enamels, and ammonium carbonate and magnesia for other enamels. Magnesium sulphate may be resorted to when nothing else will render an enamel workable. The effect of sulphates and chlorides is often obvious as white specks in coloured enamels, and is the usual explanation of enamelled ware turning dull after a day or two. With the exception of magnesia, the salts should all be made up in dilute solution in water, and added just before using the enamel by some responsible person. The whole quantity of enamel will then require thorough stirring and quite probably re-sieving. It is common knowledge that the effect of these additions passes within a few hours.

CHAPTER V.

TIN OXIDE AND ITS SUBSTITUTES.

WITH the possible exception of cobalt oxide, tin oxide is the most interesting ingredient in the enameller's recipe. The two factors accounting for its importance are :—

(*a*) The dominating influence exerted by tin oxide in white enamels, and

(*b*) The high and fluctuating cost of the material.

It must be explained at the outset that good white enamels are prepared containing no tin oxide, but the general experience of enamellers after being driven by despair at the price of tin oxide to experiment with substitutes, is despair once more, and they find that there is nothing comparable with a first-class tin enamel, which can be produced and worked economically. The average tin-less enamel requires two thick coats involving more labour charges, and more enamel; it is easily chipped and less durable. For presentable one-coat work, tin oxide is indispensable. Some substitutes render excellent service as a partial substitute for tin oxide, and these are considered later. The importance of tin oxide may be gathered from the customary definition of an enamel as an " opaque glaze containing tin oxide." During recent years the market price has steadily advanced, the variation during the past four years being from £200 to £330 per ton, but so vital is this one item that the expenditure on it may equal or even exceed that on the remainder of the chemicals in a works where white enamel predominates. Since the quantity of tin ore available is known to be limited, a general upward tendency in price appears inevitable. The numerous substitutes which have been introduced have not so far affected the situation fundamentally; their opacifying qualities in general are not in proportion to their cost, or for domestic ware they fail to pass the regulations appertaining to hygiene in many of the European countries, and often practical difficulties are experienced when introducing such materials.

Tin oxide (more correctly tin dioxide, SnO_2, M.W. 151, since another oxide, tin monoxide, SnO, which is black, exists) appears on the market as a white powder generally graded as light or heavy, though the density extends over a wide range, and a divergence of opinion exists as to the most suitable grade for enamelling purposes, the verdict generally going in favour of the lightest possible obtainable.

Its origin is the mineral *cassiterite* or *tin stone*, an ore agreeing very nearly with the chemical composition of tin dioxide. The mineral is not widely distributed, but occurs in large masses in Cornwall, the Malay Straits, and South America. Historically the Cornwall deposits are the most interesting, being regarded as an attraction for Caesar's invasion of the British Isles; St. Michael's Mount, near Penzance, was the point to which the inhabitants were reputed to have carried their tin for protection. To-day the Cornish mines can only function commercially during boom periods such as that of the coal strike, 1926. Most of the tin oxide for the English market comes from the Malay Straits. Although cassiterite is virtually impure tin oxide, no direct process of purification is possible, tin oxide being such a difficult material to treat chemically, since it is an inert and very insoluble substance. Advantage is taken of its one weakness—namely, the possibility of reducing it by heating with coke to metallic tin, which being easily melted (M.P. 232° C.) can be run off into moulds. As a preliminary, the ore is sorted, washed, and roasted to burn off arsenic and sulphur, the most likely impurities, and then reduced with coke. Metallic tin reaches a high state of purity, in which state it is usually purchased by the home manufacturer, who roasts it in a plentiful supply of air to reproduce tin oxide. The English process is carried out in the usual type of reverberatory furnace, the tin oxide being volatile, passes off and is collected. Close control is essential to reduce wastage of tin in the first process, and to obtain a complete and not merely surface oxidation in the second. A modern effort is to complete the two firings in one furnace at one operation.

A continental industry of no mean proportions deals with the detinning of scrap tinned-iron goods. This scrap is washed in a soda bath to remove grease, is rinsed in water, and heated to remove any solder, and then treated in cooled iron cylinders with chlorine gas to produce tin chloride. From this the tin may be recovered, usually electrolytically, while the steel, containing less than 0·1 per cent. tin, is pressed and sent to the steel-making furnaces. This has been a commercial process for the supply of tin and tin salts for many years, but owing to difficulties during the production of the tin and the fact that the presence of iron in the tin oxide would ruin it as far as use in enamelling is concerned, this method of preparation has not supplanted the original one of using natural tin. Tin oxide made from scrap may usually be distinguished by its slightly yellow tinge.

Tin oxide is available in a high state of purity—that is, exceeding 99·5 per cent. Its examination is work for a qualified chemist, and tin oxide, together with felspar and cobalt oxide, should be periodically subjected to this examination. A useful test for tin oxide, easily applied, is to shake a quantity up with water and allow to settle. Black particles of the metal or the lower oxide, if present, will settle to the bottom first, being heavier than the white oxide, and may be readily seen this way, a rough idea being obtained of the proportion present. Their presence indicates incomplete burning—that is, surface oxidation—and leads to black specks or holes in the finished enamel. Any appreciable quantity should lead to the rejection of the consignment. The fault may be overcome by spreading out the material in a thin layer and igniting in a furnace through which a good supply of air is passing. Where other impurities occur it is usually a result of deliberate adulteration, one sample coming under observation being found to contain zinc oxide.

Tin oxide finds employment in enamelling almost entirely as an opacifier for white enamels, though another use exists in the production of a pink pigment when used in conjunction with chromium compounds. For the former purpose tin oxide should never be added to the other materials for melting, since it will be attacked by the fluxes, and at least the first 3 per cent. added rendered valueless, either forming a transparent stannate or else a tin silicate of little or no opacifying value. When added to the mill it only comes in contact with the other ingredients during the few minutes of fusing, consequently the possibility of combination is enormously reduced, though the effect may be seen in an over-fired piece of ware. The opacifying effect of tin oxide depends upon its being evenly and very finely distributed throughout the whole mass. The percentage employed depends entirely on the class of work being produced, less than

5 per cent. is of very little service, and to produce passable results, up to 8 per cent. in two coats is required, and 12 per cent. or more where one coat white is employed. Since the tin oxide does not decompose, there is no loss on melting, and 100 per cent. yield is obtained. Tin oxide cannot be applied direct to the steel surface owing to reduction by the carbon, producing a series of blisters.

In addition to its being the finest opacifying medium, tin oxide produces a brilliant and peculiar lustre, which may possibly be equalled but never exceeded by its rivals. It has a marked effect on reducing the expansion of the enamel, and where excessive amounts appear must be compensated for by increased fluxes. The general effect of additions of tin oxide to an enamel must be to harden it, though Vielhaber claims a lowering of 50° C. in the fusing temperature by the addition of from 3 to 6 per cent. at the mill. Tin oxide is insoluble in water, and extremely resistant to all the chemicals likely to be encountered by a normal enamelled article.

The effect of the high price of the material may be realised easily when it is considered that the remaining materials of an enamelling recipe average about 2d. per lb., whereas if 7½ per cent. tin oxide is added at 2s. 6d. per lb. (£280 per ton) the price is doubled. This is only one side of the problem, the other being the wide fluctuations in price which are sufficient to upset the costing system, as a £50 increase per ton of tin oxide, which is by no means uncommon in the short space of a few months, will raise the price of the finished enamel ½d. per lb. Common sense may occasionally foresee a rise in prices, such as following industrial upheavals, and a general study of statistics may supply the necessary hint where changes are due to more involved or obscure causes, but in general they appear to be governed by considerations little more stable than wild speculation on an international scale, and anything in the nature of buying above requirements by the enameller not deeply versed in financial finesse appears to be gambling with the dice loaded heavily in the favour of the knowledge, experience, and capital of the tin syndicates.

There is little or no protection against these fluctuations by buying the metal tin and oxidising it oneself, because the price variations apply to the metal, the ratio of metal to oxide being fairly constant. The price of the oxide is usually about £20 per ton above metal price, though when competition has been keen in the past it has fallen to metal price or even below, it being remembered that 100 tons of metal theoretically make 122 tons of oxide. The manufacture of tin oxide in the enamel works is not to be recommended. It involves appreciable capital, and anything but the pure white tin oxide is useless. Considerable losses result during the manufacture under any but the tightest control, and in the long run it will prove cheaper to buy from the specialised manufacturer.

Substitutes for Tin Oxide.—The foregoing reasons are sufficient to indicate why a material to replace tin oxide is highly desirable, particularly the fact that ultimately the shortage of tin with a consequent soaring price will have to be faced. At the present time, the best substitutes can generally be employed to replace 2 per cent. of the tin oxide weight for weight, without any loss in quality. As they generally cost about half the price of tin, the economy is the equivalent of reducing tin oxide 1 per cent., which in the costing example given above means a reduction in price of the finished enamel of ¼d. per lb., or about 6 per cent. The ideal substitute has yet to be discovered, but it is safe to say that more scientific and semi-scientific investigation has taken place on this question than on any other specifically enamelling problem. The substitutes to be considered are antimony oxide, bone ash, sodium antimonate, the spinels, titanium oxide, and zirconium oxide. The proprietory opacifiers are sometimes combinations of the foregoing, and often include zinc oxide in their make-up.

Antimony Oxide. — There are three oxides of antimony.

Antimony trioxide, . . .	Sb_2O_3, M.W. = 288
„ tetroxide, . .	Sb_2O_4, M.W. = 304
„ pentoxide, . .	Sb_2O_5, M.W. = 320

The last named is of no interest as such, but is used combined with soda as sodium antimonate (which see).

Antimony trioxide has a yellowish tinge, whilst the tetroxide is a dense white powder; both are found native, but are more usually obtained by roasting the metal or the sulphide. All the oxides form the tetroxide on prolonged heating in air, and this oxide has the property, like a few others mentioned, of turning yellow on heating to become white again when cold. The white tetroxide is the one generally selected for enamelling purposes. It is almost invariably fritted with the enamel and, in addition to its principal use as an opacifier for white enamels, it is a usual constituent of the white grey ground coats containing no cobalt. Antimony when properly handled produces an enamel with an excellent finish, distinguishable from tin, but nevertheless glossy and dense. Few advocate the entire replacement of tin oxide, a blending of the two materials being generally recommended. Antimony may fail when used in white enamels for gas shades and hearth plates exposed to sulphurous vapours. It is also useless in enamels containing anything above traces of lead, owing to the production of a yellow colour, consequently in cast-iron enamelling the presence of antimony may be regarded as meaning the absence of lead. Antimony can be used in ground coats where tin oxide cannot, because carbon in steel does not cause antimony to blister. On the other hand, specks of dust and dirt in a white enamel show up more prominently in an antimony enamel than in one containing tin.

In the author's hands far better results have been obtained with this substitute than with any other, and the one reason why the use of antimony oxide has not become universal for use in hollowware is because of the fear of offending hygienic scruples, the possibility of poisoning from antimony compounds having been widely discussed. Anyone further interested in the possible poisonous nature of antimony in enamel compositions is referred to the list of references at the end of these paragraphs on antimony oxide, all of which are quoted and discussed together with the results of further investigations in the author's article, "Antimony as a Constituent of Enamels," which appeared in *Chemistry and Industry* for November 5, 1926 (*i.e.*, vol. xlv., p. 815), the conclusion to which reads :—

"Whilst it would be advantageous to know more of the toxicity of small quantities of antimony, it appears that, though the amounts dissolved from enamelled surfaces may vary, the evidence available indicates the absolute safety of pure antimonic compounds in well-fritted enamels."

A word of warning must be given against the purchase of antimony oxide of unknown origin, or without analysis, since the commercial oxides always contain arsenic in varying proportions, and the use of this material is dangerous and generally unlawful. Antimony oxide has been used with success up to 10 per cent. in the frit, the soda and nitrate being increased accordingly. It is a refractory ingredient, brings the expansion of the enamel nearer that of iron, and advantageously adds to the viscosity of the enamel batch, thus reducing the liability to devitrification. It undergoes no appreciable loss on ignition. Its insolubility in water and general resistance to dilute acids are also in its favour. The main source of antimony ores being China, the price of the oxide has varied recently owing to the trouble there, recent quotations for the proprietary brand, "Timonox," which is pure antimony oxide (free from arsenic), ranging from £67 to £87 per ton.

References to the possible toxicity of antimony in enamels include :—

Rewald (*Chem. Ztg.*, No. 53, 1-5-24).
Bock (*Chem. Ztg.*, 1908, p. 446).
Rickmann, "The Use of Antimony Compounds for White Enamels" (*Sprechsaal*, xlv., p. 115).
Wohlegemuth and Rewald, "Physiological and Chemical Tests on Antimony Compounds for the Enamel Industry," *Sprechsaal*, 1924.
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Calcium Phosphate.—Bone ash, $Ca_3(PO_4)_2$ or $3CaO, P_2O_5$. This substance occurs naturally and also, as its name implies, can be obtained from bones, 80 to 90 per cent. of the mineral matter in them being calcium phosphate. The material is of little interest to the modern enameller, the lime content being injurious, and liable to cause blisters, and such a large quantity is required to produce any opacity that the resulting enamel is difficult to melt, is brittle, readily chipped, and has a dull finish. In order to overcome the difficulty of melting, with its consequent loss of opacity, tests were made on the enamels shown in Grünwald's "Raw Materials for Enamel Industry," p. 129, in which two frits are employed, one containing the lime, the other the phosphates, with the intention of forming the calcium phosphate in the enamel during the fusing process. The results were not satisfactory. Bone ash is generally a greyish-looking powder, the bone burning industry being of large proportions, as bone ash is converted into superphospate of lime by treating with sulphuric acid, which is employed as a fertiliser.

Sodium Antimonate, $NaSbO_3$ or Na_2O, Sb_2O_5. M.W. 191. This is a compound of soda and antimonic oxide, and is prepared by the fusion of the sulphide with Chili saltpetre. Sodium antimonate as required for enamelling appears as a white powder, and its use in enamels and the effects produced are identical with those of antimony oxide, which it replaces, with the distinction that soda is always simultaneously introduced, rendering the enamel softer, and giving a higher expansion than when the oxide is used. It must be borne in mind that, whilst the oxide contains 79 per cent. of antimony, this substance contains 63 per cent., and the value as an opacifier depends on the antimony content. The price of the sodium antimonate is appreciably higher than the oxide, recent prices being about £140 per ton, and consequently the price per unit of antimony is at least double. Its one advantage is that, being combined with a flux, it may be introduced into enamels without the violent disturbance of the formula occasioned when the oxide is used ; further, it may be used up to 2 or 3 per cent. as a mill addition, though in this case it is more liable to be dissolved out. There is no loss in weight of this material during melting, and some investigators have endeavoured to demonstrate that sodium antimonate may be non-poisonous in enamels under conditions in which the oxide would be. Pure sodium antimonate, free from arsenic and other impurities, is available in " Leukonin," the patented material of Drs. Rickmann and Rappe, of Cologne. Because of its source, commercial sodium antimonate, like antimony oxide, is liable to contain sulphur, chloride, and sulphate, besides arsenic, all of which are objectionable.

Rutile.—*See* Titanium Oxide.

Spinel.—The *spinels* are compounds of the metallic oxides and alumina. The only two of interest to enamellers are the zinc and magnesium spinels, which have the compositions $ZnO . Al_2O_3$, and $MgO . Al_2O_3$. They are artificial substances made at a high temperature, and as opacifiers for enamels are usually associated with tin oxide or one of the other substitutes, since they are seldom very successful by themselves. Their efficiency depends upon the treatment they have received, since high temperatures are necessary for success, and many of those so far available are insufficiently ignited and consequently are absorbed by the enamels without yielding opacity. The zinc spinel is the more common, but both are non-poisonous and from good white enamels. When used at high percentages the enamel is difficult to fuse.

Titanium Oxide.—Titania, TiO_2. M.W. 80. Melting point, 1,560° C. Titanium occurs naturally as the mineral *rutile* in America and Bavaria, the ore being composed of the crude oxide and iron impurities. It also occurs combined with iron in *ilmenite* or titanic iron ore, $FeTiO_3$. In the pure state, when it is a white powder, it resembles silica in many respects, being unattacked by acids and being infusible. This makes it difficult to purify, and it is the cost of this purification which has acted against its popularity in the past. Unless it is absolutely freed from iron, it is useless for the purpose of an opacifier for white enamels, and its future, like that of zirconia, discussed below, depends upon an economic process of purification. It undergoes no loss of weight on heating, and is absolutely non-poisonous, and it is this latter quality which renders it attractive. Its price depends entirely on its purity, and it generally appears on the market under trade names, often being associated with zirconia, tin oxide, or other opacifiers, when it is priced at a figure which should be attractive against tin oxide. It is preferable to use it at the mill like tin oxide, and not frit it, as part will be dissolved without yielding opacity. Titania yields quite a good dense white enamel, has an expansion just greater than that of iron, and consequently is superior to tin oxide in this respect. Like some of the other opacifiers, titania is used in the paint industry as a white pigment, and here it is usual to mix with it a little calcium phosphate to compensate for creaminess in the titanium.

Zirconium Oxide.—*Zirconia*, ZrO_2. M.W. 123. This occurs naturally as the silicate ore, *zircon*, $ZrSiO_4$, which s discoloured by iron, the chemically pure zirconia being white ; zirconia is extremely infusible, and consequently is used for crucibles in which platinum or silica may be melted without the destruction of the zirconia. Another favourable property for this purpose is its very ow expansion. In enamels it is used exactly as tin oxide, and produces a very good opaque effect, though in numerous investigations as good a result as that obtained from antimony oxide has not been obtained, though samples seen from other quarters and duly authenticated have been as good as antimony and a near approach to tin oxide samples ; zirconia is absolutely non-poisonous, and in the writer's opinion shows the most promise of all the opacifiers. The difficulty in placing zirconia on the market at a competitive price is the necessity of obtaining a high state of purity, and the difficulty of attaining this object. The obstacle is the same as in the case of titanium, the removal of iron compounds. Of the advantages it possesses over tin oxide and antimony oxide must be mentioned its resistance to the reducing gases of the furnace, with consequent elimination of the possibility of black specks or holes due to the formation of metal. Claims are also made that it increases the resistance of the enamel to acid, impact, and sudden temperature change. Additions to the frit will render it more viscous, but increase the time of melting, and the first 3 or 4 per cent. added will be dissolved and produce no opacity. Zirconia suffers no loss on heating, and gives an excellent lustre. Like most new ingredients, it has its peculiarities, and a certain amount of experimenting is necessary to produce the best results. One such peculiarity is its production of a very "short" enamel, which when disturbed tends to move about in clots. In this condition it is difficult to produce a uniform coating on an article. With many clays, salt additions can be omitted when using zirconia, and a lower proportion of clay employed. Like the other opacifiers, zirconia appears under a variety of trade names, and associated with titania and tin oxide. Its price varies from £140 to £220 per ton, according to its composition.

Some comparative tests on opacifiers have been reported by Danielson and Frehafer,* who placed these in order of merit :—Zirconia, sodium antimonate (neither very inferior to tin oxide), and zirconium silicate third. The others tested were titania and the spinels.

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* *J. Amer. Cer. Soc.*, 1923, vi., 634.

CHAPTER VI.

THE CALCULATION OF BATCH FORMULÆ AND PHYSICAL PROPERTIES OF ENAMELS.

SINCE most formulæ are confined to the same few raw materials, it is possible by familiarity to judge an enamel by the composition of the original mixture. This is purely approximate, however, and the only satisfactory method is a consideration of the chemical composition after firing, and this is necessary for any systematic work involving the alteration of the constitution of the enamel, or its various physical properties, such as expansion, etc. The complete analysis of a fused enamel is a long and tedious operation, and is work for not only a skilled but specialised chemist, and as a routine operation is both impracticable and unnecessary where the raw materials are known, because the analysis may be calculated with sufficient accuracy.

It is common knowledge that in melting an enamel from 20 to 30 per cent. by weight is lost in vapour up the flues, roughly half the borax and soda being lost, two-thirds of the nitrate, and small proportions of the other ingredients. Before this loss may be calculated with any degree of exactness, an understanding of the composition of the various materials is necessary.

Following each of the names of substances in the preceding chapters, the chemical formula was given, which is in reality a form of shorthand, chemists having assigned to each element a symbol, often the first letter of its name, for example B for boron and O for oxygen ; but this symbol means more, it indicates the relative or atomic weight of the element concerned, thus B means 11 parts by weight of boron, O means 16 of oxygen (hydrogen being the lightest of the elements is taken as 1). Table V. shows the elements commonly met with in enamelling, together with their symbols and atomic weights. Compounds, which, of course, are built up from elements, are represented by writing the symbols for the elements alongside one another, in the proportions in which they are present. Thus silica (quartz, flint, or sand), which contains one atom of silicon and two of oxygen, is written SiO_2, and its molecular weight is $28 + (16 \times 2) = 60$, the sum of atomic weights being called the molecular weight. The more complicated molecules, such as felspar, $K_2Al_2Si_6O_{16}$, may be rewritten in a simpler or empirical form (that is, in the manner in which they would be identified by analysis), thus $K_2O, Al_2O_3, 6SiO_2$, the various parts of this, the potassium oxide, alumina, and silica being known as radicles. Most compounds used in enamelling belong to that large class of substances known chemically as salts—that is, compounds formed by combining acids with bases—the

TABLE V.

Element.	Symbol.	At. Wt.	Element.	Symbol.	At. Wt.
Aluminium, .	Al	27	Manganese, . .	Mn	55
Antimony, . .	Sb	120	Nickel, . .	Ni	59
Barium, . .	Ba	137	Nitrogen, . .	N	14
Boron, . .	B	11	Oxygen, . .	O	16
Calcium, . .	Ca	40	Potassium, . .	K	39
Carbon, .	C	12	Silicon, . .	Si	28
Chromium, . .	Cr	52	Sodium, . .	Na	23
Cobalt, . .	Co	59	Sulphur, . .	S	32
Fluorine, . .	F	19	Tin, . . .	Sn	119
Hydrogen, . .	H	1	Titanium, . .	Ti	48
Iron, . . .	Fe	56	Zinc, . . .	Zn	65
Magnesium, .	Mg	24	Zirconium, . .	Zr	91

acids being derived from the oxides of the non-metals—that is, the refractories in the enamel—whilst the bases are the metallic oxides, or the fluxes in the enamel; thus K_2O is the basic part and SiO_2 the acidic part of felspar. Again, the formula for crystalline borax is $Na_2H_{20}B_4O_{17}$, though it is never so written, appearing always as $Na_2B_4O_7$, $10H_2O$. The H_2O (*i.e.*, water) is always grouped together, because it is a common constituent of crystalline substances, and is known as "water of crystallisation," being removed on heating and having no influence on the chemical properties of the substance to which it is attached. The important part of borax is $Na_2B_4O_7$, which may be rewritten $Na_2O, 2B_2O_3$, showing the basic soda, and the acidic boron oxide. The molecular weight of borax (382) is calculated simply by adding together all the atomic weights, thus:—

$$\begin{aligned} Na_2B_4O_7, 10H_2O &= Na_2O, 2B_2O_3, 10H_2O \\ &= (23 \times 2 + 16) + 2(11 \times 2 + 16 \times 3) + 10(1 \times 2 + 16) \\ &= 62 + 2(70) + 10(18) \\ &= 62 + 140 + 180 \\ &= 382 \end{aligned}$$

To calculate from this the percentage of soda, boric oxide, and water obtained from 100 lbs. of borax is just simple arithmetic with these figures.

Thus, from the above figures, we see that every 382 parts by weight of borax contain 62 of sodium oxide (Na_2O), 140 of boric oxide (B_2O_3), and 180 of water.

Hence the Na_2O from 100 lbs. of borax is—

$$\frac{100 \times 62}{382} = 16{\cdot}3 \text{ per cent.}$$

The B_2O_3 is $\frac{100 \times 140}{382} = 36{\cdot}6$ „

And the water $\frac{100 \times 180}{382} = 47{\cdot}1$ „

Total, . . $100{\cdot}0$ „

These percentages, obtained by calculation, are the same as would be obtained by a chemical analysis of the pure substance.

Table VI. is drawn up to show all the usual enamelling materials, with their true chemical names and molecular weights. The percentages of the various radicles obtained from 100 parts by weight of them are also given, the bases and acids being kept together, and those which are lost during melting being distinguished from those which remain in the enamel. Thus, in the case of borax, 47·1 per cent. passes away, leaving 52·9 per cent. of the original weight in the enamel.

From this table it is possible to calculate the loss in melting an enamel. Take the imaginary formula :—

Borax,	20	per cent.
Cryolite,	12	,,
Felspar,	30	,,
Quartz,	30	,,
Sodium carbonate,	5	,,
Sodium nitrate,	3	,,
	100	,,

Noting from the table the total weights retained and lost, we find that from—

20	parts of	borax,	10·6	are retained.
12	,,	cryolite,	12·5	,,
30	,,	felspar,	30·0	,,
30	,,	quartz,	30·0	,,
5	,,	soda,	2·9	,,
3	,,	nitrate,	1·1	,,
100	,,	moisture,	87·1	,,

or a theoretical loss of 12·9 per cent. results. The figure is low in this case owing to the high proportion of felspar

MATERIAL.	CHEMICAL NAME.	FORMULA.	MOLECULAR WEIGHT.	RETAINED AFTER MELTING.														LOST ON MELTING (per cent.).
				Bases (per cent.).								Al_2O_3 (per cent.).	Acids (per cent.).			Special Components (per cent.).	Total Weight Retained (per cent.).	
				Na_2O.	K_2O.	CaO.	MgO.	BaO.	CoO.	MnO.	NiO.		SiO_2.	B_2O_3.	F.			
Alum, . . .	Potassium Aluminium Sulphate,	$K_2SO_4,Al_2(SO_4)_3,24H_2O$	948	..	9·9	..	..	..	..	..	..	10·7	..	..	..	..	20·6	79·4 H_2O+SO_3
Ammonium Carbonate,	. . . .	A mixture, $N_3H_{11}C_2O_5$	157	..	..	..	..	..	..	..	..	..	..	..	..	..	..	100 $NH_3+CO_2+H_2O$
Antimony Oxide, .	Antimony Tetroxide, . .	Sb_2O_4	306	..	..	..	..	..	..	..	..	..	..	..	..	105·2 Sb_2O_5	105·2	..
Artificial Cryolite, .	Sodium Silico-Fluoride, . .	Na_2SiF_6	188	33·0	..	..	..	..	..	..	..	..	31·9	..	60·6	..	125·5	30·3 F_2
Barium Carbonate, .	. . . .	$BaCO_3$	197	..	..	..	..	77·7	..	..	..	..	..	..	..	..	77·7	22·3 CO_2
Boric Acid, . .	. . . .	H_3BO_3	62	..	..	..	..	..	..	..	..	..	..	56·5	..	..	56·5	43·5 H_2O
Borax, . . .	Sodium Pyroborate, . .	$Na_2B_4O_7,10H_2O$	382	16·3	..	..	..	..	..	..	..	..	..	36·6	..	..	52·9	47·1 H_2O
Calcspar, . . .	Calcium Carbonate, . .	$CaCO_3$	100	..	..	56·0	..	..	..	..	..	..	..	..	..	..	56·0	44·0 CO_2
Chili Saltpetre, . .	Sodium Nitrate, . . .	$NaNO_3$	85	36·5	..	..	..	..	..	..	..	..	..	..	..	..	36·5	63·5 N_2O_5
Chromium Oxide, .	. . . .	Cr_2O_3	152	..	..	..	..	..	..	..	..	..	..	..	..	100 Cr_2O_3	100·0	..
Clay, . . .	Aluminium Silicate, . .	$Al_2O_3,2SiO_2,2H_2O$	252	..	..	..	..	..	..	..	..	39·6	46·5	..	..	..	86·1	13·9 H_2O
Black Cobalt Oxide, .	Tricobaltic Tetroxide, . .	Co_3O_4	241	..	..	..	..	..	93·4	..	..	..	..	..	..	..	93·4	6·6 O_2
Grey Cobalt Oxide, .	Cobaltous Oxide, . . .	CoO	75	..	..	..	..	..	100·0	..	..	..	..	..	..	..	100·0	..
Cryolite, . . .	Sodium Aluminium Fluoride, .	Na_3AlF_6	420	44·3	..	..	..	..	..	..	..	24·3	..	..	36·2	..	104·8	18·1 F_2
Felspar, . . .	Potassium Aluminium Silicate, .	$K_2O,Al_2O_3,6SiO_2$	556	..	16·9	..	..	..	..	..	..	18·3	64·8	..	..	..	100·0	..
Flint, . . .	Silica, ...	SiO_2	60	..	..	..	..	..	..	..	..	..	100·0	..	..	..	100·0	..
Fluorspar, . .	Calcium Fluoride, . . .	CaF_2	78	..	..	71·8	..	..	..	..	..	..	..	..	36·5	..	108·3	12·2 F_2
Iron Chromate, . .	Ferrous Chromate, . . .	$FeCrO_4$	172	..	..	..	..	..	..	..	..	..	..	..	..	41·8 FeO, 58·2 CrO_3	100·0	..
Black Iron Oxide, . .	Ferroso-ferric Oxide, . .	Fe_3O_4	232	..	..	..	..	..	..	..	..	..	..	..	..	103·5 Fe_2O_3	103·5	..
Red Iron Oxide, .	Ferric Oxide, ...	Fe_2O_3	160	..	..	..	..	..	..	..	..	..	..	..	..	100 Fe_2O_3	100·0	..
Magnesia, . . .	Magnesium Oxide, . . .	MgO	40	..	..	..	100·0	..	..	..	..	..	..	..	..	..	100·0	..
Magnesium Carbonate,	. . . .	$MgCO_3$	84	..	..	..	47·6	..	..	..	..	..	..	..	..	..	47·6	52·4 CO_2
Black Nickel Oxide, .	Nickel Sesquioxide, . .	Ni_2O_3	166	..	..	..	..	..	..	..	90·4	..	..	..	..	..	90·4	..
Grey Nickel Oxide, .	Nickelous Oxide, . . .	NiO	75	..	..	..	..	..	..	..	100·0	..	..	..	..	..	100·0	..
Pearl Ash, . .	Potassium Carbonate, . .	K_2CO_3	138	..	68·1	..	..	..	..	..	..	..	..	..	..	..	68·1	31·9 CO_2
Pyrolusite, . .	Manganese Dioxide, . .	MnO_2	87	..	..	..	..	..	..	81·5	..	..	..	..	..	..	81·5	18·5 O_2
Quartz, . . .	Silica, ...	SiO_2	60	..	..	..	..	..	..	..	..	..	100·0	..	..	..	100·0	..
Saltpetre, . . .	Potassium Nitrate, . . .	KNO_3	101	..	46·5	..	..	..	..	..	..	..	..	..	..	..	46·5	53·5 N_2O_5
Sand, . . .	Silica, ...	SiO_2	60	..	..	..	..	..	..	..	..	..	100·0	..	..	..	100·0	..
Sodium Antimonate, .	. . . .	$NaSbO_3$	191	16·3	..	..	..	..	..	..	..	..	..	..	..	83·7 Sb_2O_5	100·0	..
Soda Ash, . .	Sodium Carbonate, . . .	Na_2CO_3	106	58·5	..	..	..	..	..	..	..	..	..	..	..	..	58·5	41·5 CO_2
Sodium Nitrate, .	*See* Chili Saltpetre, . . .	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Sodium Silicofluoride, .	*See* Artificial Cryolite, . .	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Tin Oxide, . .	Stannic Oxide, ...	SnO_2	151	..	..	..	..	..	..	..	..	..	..	..	..	100 SnO_2	100·0	..
Titanium Oxide, . .	. . . .	TiO_2	80	..	..	..	..	..	..	..	..	..	..	..	..	100 TiO_2	100·0	..
Zinc Oxide, . .	. . . .	ZnO	81	..	..	..	..	..	..	..	..	..	..	..	..	100 ZnO	100·0	..
Zirconium Oxide, .	. . . .	ZrO_2	123	..	..	..	..	..	..	..	..	..	..	..	..	100 ZrO_2	100·0	..

and quartz, for which no loss is shown. Various factors, which in practice upset this figure, include :—

(1) Impurities in the raw materials.
(2) Draught through the furnace blowing away part of the lighter material.
(3) Varying conditions in the melter—*i.e.*, oxidising or reducing atmosphere, temperature too hot or too cold.
(4) Brickwork of furnace dissolving and entering the batch.
(5) A portion of the ingredients turning to vapour at the furnace temperature.
(6) Moisture adhering to the frit when weighing the yield.
(7) Losses due to handling, etc.

A further comment necessary on the calculation and the table is the observation that some of the materials are shown to gain in weight on melting, the most notorious being sodium silico-fluoride, Na_2SiF_6. The reason for this is that it is assumed to take up the oxygen from that being provided in the furnace by the nitrate, and from the air draughts, to produce Na_2O, SiO_2, and F. A further comment is necessary on the action of all fluorine-containing substances. The bulk of the fluorine is retained in the enamel, but part is lost. This latter has been denied, but chemical analysis establishes the fact that part vaporises away. The proportion lost depends entirely on furnace conditions, and the composition of the enamel, but as the percentage of fluorine compounds is never high, it is simplest to accept Grünwald's figures, which are an excellent approximation ; he states that one-quarter of the fluorine in fluorspar is lost, and one-third in cryolite, and to this may be added one-third in the case of sodium silico-fluoride. Thus from every 100 lbs. of fluorspar 12·2 per cent. of fluorine is lost, from 100 lbs. of cryolite 18·1 per cent., and from sodium silico-fluoride 30·3 per cent. The fluorine is assumed to pass away in the form of the gas silicon fluoride, which further involves the loss of some silica, thus :—

$$\begin{array}{cccccc} SiO_2 & + \; 2CaF_2 & = & SiF_4 & + & 2CaO. \\ \text{Silica} & \text{Fluorspar} & & \text{Silicon fluoride} & & \text{Lime.} \\ 60 & + \; 156 & & & & \end{array}$$

Thus 156 parts of fluorspar which contain 76 of fluorine destroy 60 parts of silica, hence 12·2 parts of fluorine destroy 9·6 of silica, and consequently for every 100 lbs. of fluorspar in the original batch 9·6 lbs. of silica are lost ; similarly for every 100 lbs. of cryolite 14·3 lbs. of silica are lost, or roughly 10 per cent. of the weight of the fluorine-containing substances. This quantity is so trivial that it need not be taken into account. Fluorine is always assumed to volatilise as silicon fluoride, though the conditions may be favourable for the formation of boron fluoride, which is also a gas.

A further useful application arises from Table VI., and that is to reverse the calculation we have used to work out an analysis being given the formula, and to calculate a formula from a given analysis :—

As an example, a compound may be found to have the analysis :—

K_2O, ...	16·9	per cent.
Al_2O_3, ...	18·3	„
SiO_2, ...	64·8	„
	100·0	„

The weight of one molecule of K_2O is $39 \times 2 + 16 = 94$. Therefore, the number of molecules present is

$$16{\cdot}9 \div 94 = 0{\cdot}18.$$

Similarly the molecular weight of Al_2O_3 is $27 \times 2 + 3 = 102$, and the number of molecules is

$$18{\cdot}3 \div 102 = 0{\cdot}18.$$

In the case of SiO_2 it is $64{\cdot}8 + 60 = 1{\cdot}08$.

The proportion of K_2O to Al_2O_3 to SiO_2 is, therefore,

$$0{\cdot}18 : 0{\cdot}18 : 1{\cdot}08$$

or

$$1 : 1 : 6$$

Consequently the formula is K_2O, Al_2O_3, $6SiO_2$, which is felspar.

Calculated Analysis of Final Enamel.—To obtain the analysis of the enamel, it is only necessary to refer again to Table VI., and enter the various radicles obtained from each ingredient in columns and total up. Keeping to the same formula we obtain :—

TABLE VII.

Raw Material.		Na_2O.	K_2O.	Al_2O_3.	SiO_2.	B_2O_3.	F_2.
20	Borax, . .	3·3	...	...	...	7·3	...
12	Cryolite, . .	5·3	...	2·9	...	...	4·3
30	Felspar, . .	...	5·1	5·5	19·4	...	...
30	Quartz, . .	...	...	...	30·0	...	...
5	Soda, . .	2·9	...	...	...	...	...
3	Nitrate, . .	1·1	...	...	...	...	..
100		12·6	5·1	8·4	49·4	7·3	4·3

Total, 87·1.

Hence in 87·1 lbs. of enamel there are 12·6 lbs. of Na_2O, and, therefore, the percentage is

$$\frac{100 \times 12{\cdot}6}{87{\cdot}1} = 14{\cdot}5.$$

And the whole analysis is

Na_2O, ...	14·5	per cent.
K_2O, ...	5·9	,,
Al_2O_3, ...	9·5	,,
SiO_2, ...	56·8	,,
B_2O_3, ...	8·4	,,
F_2, ...	4·9	,,
	100·0	,,

This corresponds to the result obtainable by chemical analysis, and is achieved by simple calculation alone. The mill additions such as clay and tin oxide have been omitted, and the frit portion of the enamel only considered because this is the usual proceeding. Mill additions are generally very similar, and it is general practice to compare and contrast frits rather than the final enamel. When the latter is required, however, the procedure is exactly the same. A question frequently asked is whether, knowing this analysis, it is possible to reconstruct the original formula. The answer is a modified negative. It is shown in the example given that the soda radicle Na_2O is obtained from four sources, making a total of 14·5 per cent., but whether this is all obtained from soda ash, or cryolite, or how much from either, is not indicated at all. Hence it is impossible to reconstruct with any degree of certainty. An experienced man, however, bearing in mind the usual limits of the raw materials, might after a certain amount of juggling and practical trials successfully produce a similar enamel.

The composition of an enamel frit is seldom left in the form of the analytical table given above, since for comparison purposes it is advantageous to group some of the ingredients together; this again involves arithmetic only, using the analysis as a basis. The method most widely adopted is similar to that used for comparing glasses, and instead of expressing the composition in percentages by weight, the number of molecules of each is calculated in a manner similar to that shown on p. 105. Thus, taking the 14·5 per cent. of Na_2O present, the molecular weight of this is $23 \times 2 + 16 = 62$. Therefore, the number of molecules present is $\frac{14 \cdot 5}{62} = 0 \cdot 234$.

Carrying out this procedure for all the radicles, the result obtained is :—

Na_2O,	0·234
K_2O,	0·063
Al_2O_3,	0·093
SiO_2,	0·947
B_2O_3,	0·120
F_2,	0·129

Where glasses are concerned it is usual to group together the metals forming similar oxides ; thus all which have two parts of metal combined with one of oxygen are arranged together in a group known as R_2O, those with one of metal to one of oxygen as RO, and so on.

Thus glasses may read :—

	R_2O	RO	RO_2
	Na_2O	CaO	6 SiO_2
or	1·2 Na_2O	CaO	8·6 SiO_2

For enamels all the fluxing oxides are grouped together, and all the refractories (including fluorine). Alumina is classed by itself, thus :—

Na_2O,	0·234	Al_2O_3, 0·093	$SiO_2 = 0·947$
K_2O,	0·063		$B_2O_3 = 0·120$
	0·297		$F_2 = 0·129$

For comparison purposes the total of the fluxing oxides is made up to unity, and the other ingredients increased in proportion. In this case it is obtained by dividing all figures given by 0·297 :—

Na_2O,	0·787	Al_2O_3, 0·313	$SiO_2 = 3·190$
K_2O,	0·213		$B_2O_3 = 0·404$
	1·000		$F_2 = 0·434$
			4·028

It is on this basis, with the fluxing oxides totalling unity, that the composition of enamels is now universally expressed. Thus we read that for steel enamels CaO should not exceed 0·1, alumina content for cast-iron whites should be between 0·1 and 0·25, and so on. The comparison is still not absolutely fair, since one part of Na_2O is equivalent to about one and a half parts of K_2O, and consequently in two enamels having identical compositions except that in one case all the flux is Na_2O and in the other all K_2O, the former would be softer. Nevertheless, this method is the most satisfactory means so far devised. In the example given above, the silica is unduly high, making a hard enamel, whilst the alumina is on the high side also. The following limits have been stated for steel enamels :—

GROUND COAT. 1. Vondracek,*	0·5 – 0·7 Na_2O 0·2 – 0·3 K_2O 0·3 – 0·0 CaO	0·15–0·35 Al_2O_3	2·0 – 3·1 SiO_2 0·5 – 1·1 B_2O_3 0·0 – 0·3 F_2
2. Shaw,† .	0·0 – 0·6 Na_2O 0·15–0·75 K_2O 0·14–0·64 CaO 0·0 – 0·06 CoO	0·1 – 0·5 Al_2O_3	1·1 – 1·7 SiO_2 0·2 – 0·5 B_2O_3
COVER COATS. 1. Vondracek,	0·45–0·7 Na_2O 0·15–0·3 K_2O 0·4 – 0·0 CaO	0·0 – 0·55 Al_2O_3	2·0 – 4·3 SiO_2 0·15–0·7 B_2O_3 0·0 – 0·8 F_2 0·3 SnO_2
2. Shaw, .	0·0 – 0·65 Na_2O 0·0 – 0·60 K_2O 0·2 – 0·60 CaO	0–0·5 Al_2O_3	1·0 – 1·8 SiO_2 0·2 B_2O_3
3. Shaw (white kitchen utensils), .	0·683 Na_2O 0·195 K_2O 0·122 CaO 1·000	0·34 Al_2O_3	2·315 SiO_2 0·571 B_2O_3 1·390 F_2 0·235 SnO_2 4·511

Use of Graphs.—The three graphs are given in order to eliminate the bulk of the calculation, and to enable

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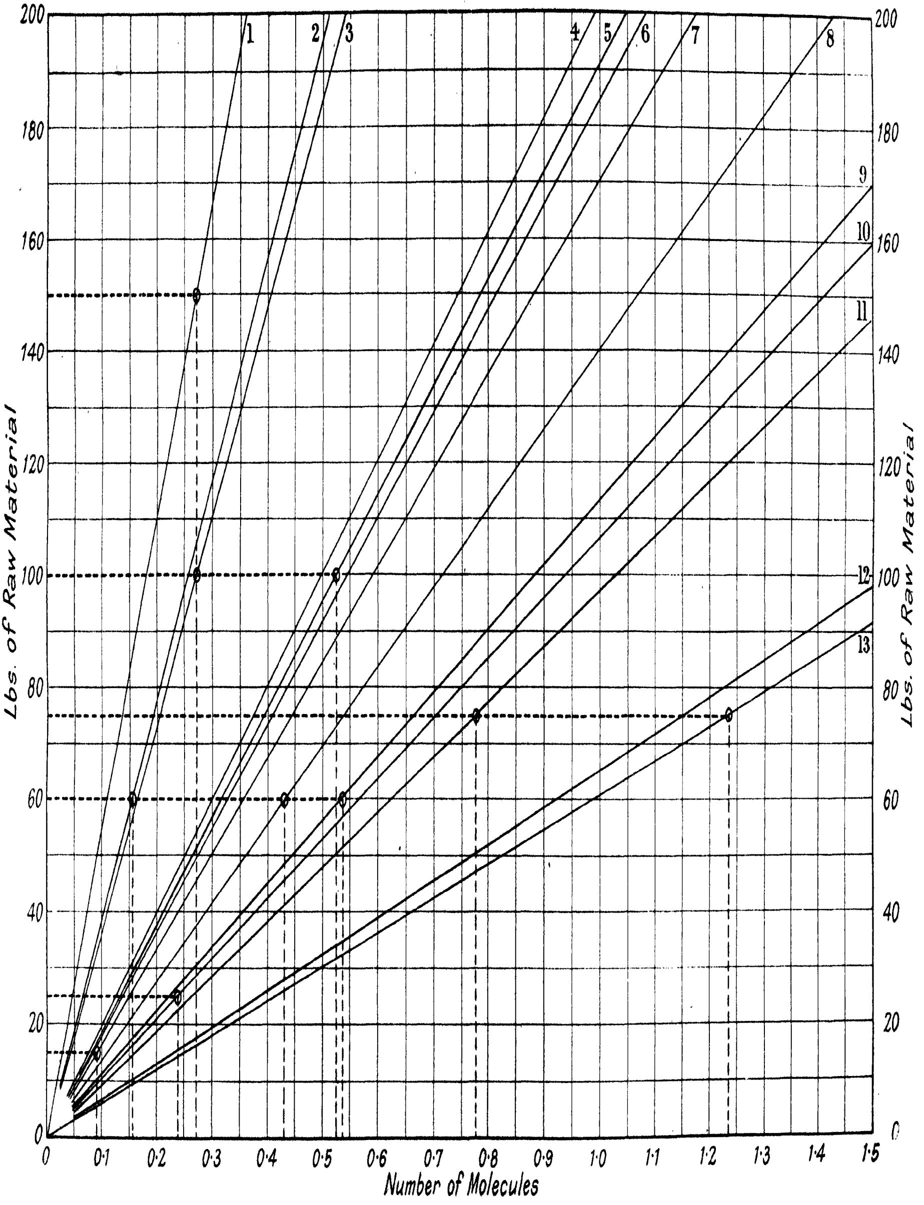
* *Sprechsaal Calendar*, 1910.

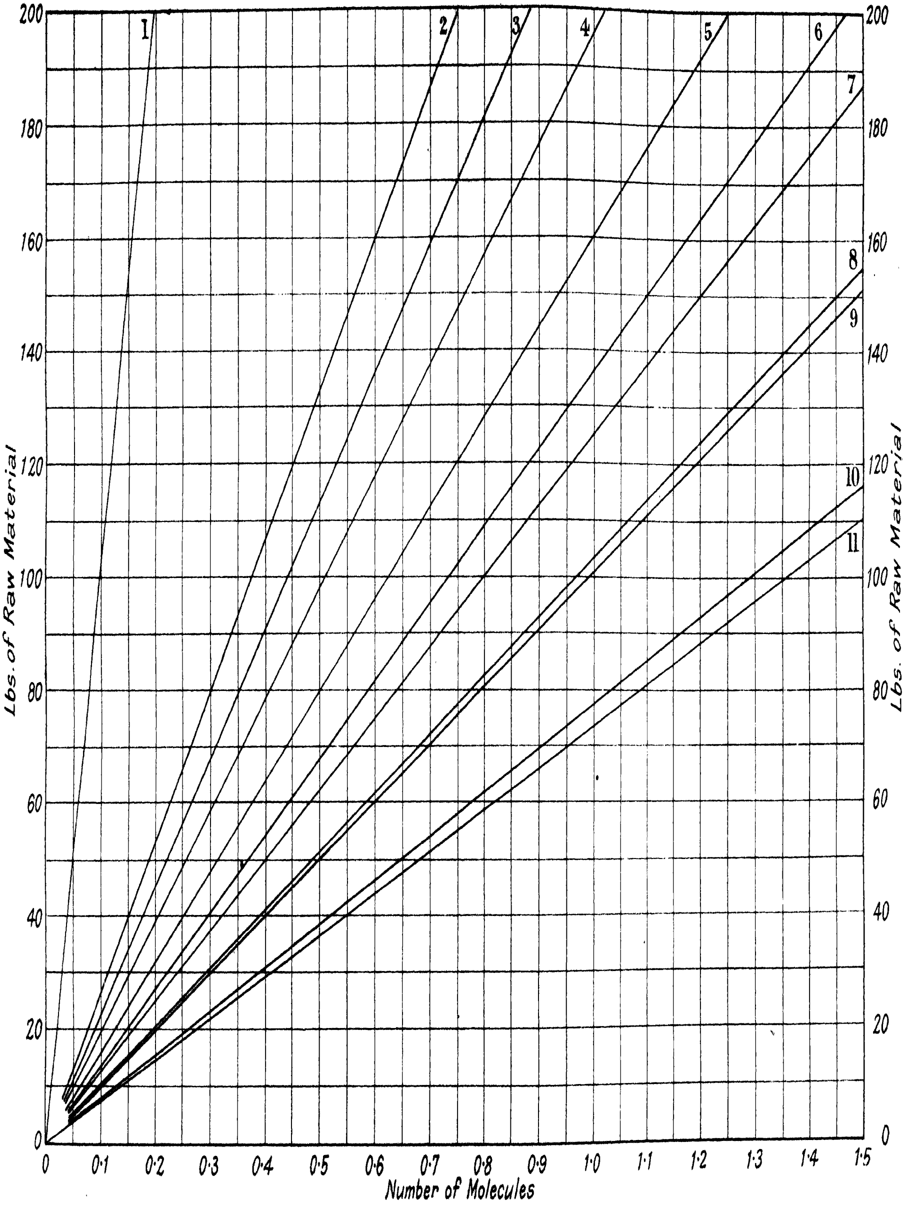
† *Trans. Amer. Cer. Soc.*, vol. xi., p. 103.

PLATE I.



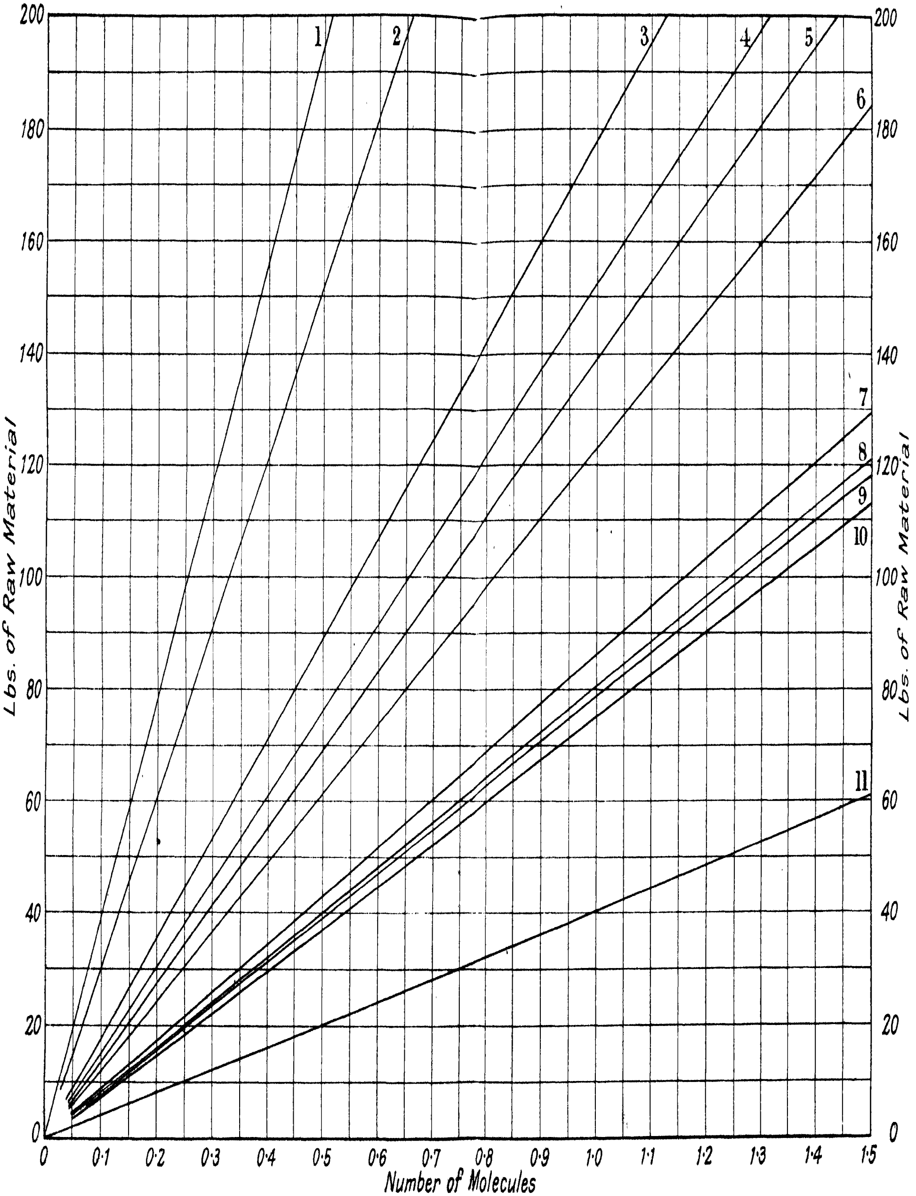
No. 1. Felspar, ... $K_2O + Al_2O_3$
No. 2. Cryolite, ... Al_2O_3
No. 3. Borax, ... Na_2O
No. 4. Pot. Nitrate, ... K_2O
No. 5. Borax, ... B_2O_3
No. 6. Sod. Silico Fluoride, . $Na_2O + SiO_2$
No. 7. Sod. Nitrate, ... Na_2O
No. 8. Cryolite, ... Na_2O
No. 9. Cryolite, ... F_2
No. 10. Sod. Carb., ... Na_2O
No. 11. Felspar, ... SiO_2
No. 12. Sod. Silico Fluoride, . F_2
No. 13. Quartz, ... SiO_2

PLATE II.



No. 1. Alum, ...	$K_2O + Al_2O_3$
No. 2. Clay, ...	Al_2O_3
No. 3. Iron Chromate, . .	$FeO + CrO_3$
No. 4. Barium Carb., . .	BaO
No. 5. Iron Oxide, . . .	Fe_2O_3
No. 6. Clay, ...	SiO_2
No. 7. Boric Acid, . . .	B_2O_3
No. 8. Fluorspar, . . .	F_2
No. 9. Calcium Carb., . .	CaO
No. 10. Fluorspar, . . .	CaO
No. 11. Cobalt Oxide, . .	CoO

PLATE III.



No. 1.	Sod. Antimonate,	$Na_2O + Sb_2O_5$
No. 2.	Antimony Oxide,	Sb_2O_4
No. 3.	Manganese Dioxide,	Mn_2O_3
No. 4.	Tin Oxide,	SnO_2
No. 5.	Pot. Carbonate,	K_2O
No. 6.	Zirconium Oxide,	ZrO_2
No. 7.	Mag. Carbonate,	MgO
No. 8.	Zinc Oxide,	ZnO
No. 9.	Titanium Oxide,	TiO_2
No. 10.	Nickel Oxide,	NiO
No. 11.	Mag. Oxide,	MgO

the composition to be read direct. The weights of raw materials are given in the vertical direction, and the number of molecules may be read immediately along the horizontal at the bottom of the diagrams. Thus, supposing a 500-lb. batch of the same enamel is being made, the original composition is :—

Borax, ...	100
Cryolite, ...	60
Felspar, ...	150
Quartz, ...	150
Soda, ...	25
Sodium nitrate, ...	15
	500

All these materials are dealt with in the first graph, and for borax it is seen that curves Nos. 3 and 5 apply. Proceeding up the left-hand side until reaching 100 (*i.e.*, the weight of raw borax), we proceed in a horizontal direction until curves 3 and 5 are crossed. A vertical is dropped from these points, and the number of molecules of Na_2O and B_2O_3 read off from the scale—namely, 0·370 Na_2O and 0·520 B_2O_3. This is done for all six substances, the points being ringed for the sake of clarity in this example. The figures obtained are :—

	Na_2O.	K_2O.	Al_2O_3.	SiO_2.	B_2O_3.	F_2.
100 Borax, . .	0·270	...	...	...	0·520	...
60 Cryolite, .	0·430	...	0·155	...	...	0·54
150 Felspar, .	...	0·270	0·270	1·500	...	...
150 Quartz, .	...	...	...	2·470	...	...
25 Soda, . .	0·240	...	...	...	...	...
15 Nitrate, .	0·090	...	...	...	...	...
Totals, .	1·030	0·270	0·425	3·970	0·520	0·54
That is,	1·030 Na_2O 0·270 K_2O 1·300		0·425 Al_2O_3		3·970 SiO_2 0·520 B_2O_3 0·540 F_2	

Reducing the fluxing oxides to unity by dividing throughout by 1·300, the composition is obtained :—

0·794 N_2O	0·327 Al_2O_3	3·060 SiO_2
0·206 K_2O		0·400 B_2O_3
		0·415 F_2
1·000		3·875

which shows reasonable agreement with the previous calculation. In this particular case the sheet is insufficiently large to show the silica equivalents of 150 lbs. of felspar and quartz direct, so the figure for 75 lbs. has been read, and doubled. Any contemplated substitution can now be carried out systematically, say, the increase of 0·1 molecule of soda with a consequent reduction of 0·1 of potash. By means of the graphs or calculation, it is possible to find readily the quantities of raw materials which must be changed.

A good practical example of the use of these tables and graphs is the substitution of sodium silico-fluoride for cryolite in an enamelling formula. Maintaining the standard example, and carrying out the substitution, the composition obtained is :—

	Na_2O.	K_2O.	Al_2O_3.	SiO_2.	B_2O_3.	F_2.
20 Borax, . . .	3·3	...	...	...	7·3	...
30 Felspar, . . .	...	5·1	5·5	19·4	...	...
30 Quartz, . . .	...	...	...	30·0	...	...
5 Sodium carbonate, .	2·9	...	...	...	...	...
3 Sodium nitrate, .	1·1	...	...	...	...	...
12 Sod. silico-fluoride, .	4·0	...	...	3·8	...	...
100 Mixture, . .	11·3	5·1	5·5	53·2	7·3	7·3
Total, . .	89·7					

The Analysis Reading.		Compared with Original Analysis.
Na_2O,	12·6	14·5
K_2O,	5·7	5·9
Al_2O_3,	6·1	9·5
SiO_2,	59·4	56·8
B_2O_3,	8·1	8·4
F_2, .	8·1	4·9
	100·0	100·0

The characteristics being a lowering of soda and alumina, and an increase of silica and fluorine.

Reading the new composition from the graphs :—

	Na_2O.	K_2O.	Al_2O_3.	SiO_2.	B_2O_3.	F_2.
100 Borax, . .	0·270	...	...	...	0·520	
150 Felspar, . .	...	0·270	0·270	1·500	...	...
150 Quartz, . .	...	...	...	2·450	...	...
25 Soda, . .	0·265	...	...	...	...	...
15 Sod. nitrate, .	0·090	...	...	...	...	...
60 Sod. silico-fluoride, .	0·355	...	...	2·355	...	0·925
500	0·890	0·270	0·270	4·305	0·520	0·925

$$\underbrace{0·890 \quad 0·270}_{1·250}$$

giving the composition :—

Na_2O, 0·785	0·215 Al_2O_3	3·440 SiO_2
K_2O, 0·215		0·416 B_2O_3
		0·740 F_2
1·000		4·596

Compared with :—

Na_2O, 0·794	0·327 Al_2O_3	3·060 SiO_2
K_2O, 0·206		0·400 B_2O_2
		0·415 F_2
1·000		3·875

To obtain the same ultimate composition using sodium silico-fluoride in place of cryolite.

Since all the fluorine is to be obtained from sodium silico-fluoride, this is the starting-out point. From Table VII., p. 105, it is seen that 4·3 lbs. of fluorine are obtained from 12 lbs. of cryolite, but from Table VI., p. 102, 100 lbs. of sodium silico-fluoride supply 60·3 lbs. of fluorine, consequently to supply 4·3 lbs. of fluorine, $\frac{100 \times 4\cdot3}{60\cdot3} = 7\cdot14$ lbs. of sodium silico-fluoride are necessary; but the introduction of this also brings in soda and silica, the quantities being:—

$$\frac{7\cdot14 \times 33\cdot0}{100} = 2\cdot38 \text{ lbs. soda,}$$

and

$$\frac{7\cdot14 \times 31\cdot9}{100} = 2\cdot27 \text{ lbs. silica.}$$

At the same time, 5·3 lbs. of soda and 2·9 lbs. of alumina have been lost by the absence of the cryolite, consequently there is a net loss of 2·92 lbs. of soda, and 2·9 lbs. alumina, and a gain of 2·27 lbs. of silica. The first and third of these can be rectified immediately, but the alumina must either be introduced as felspar or china clay. In the former case $\frac{100 \times 2\cdot9}{18\cdot3} = 15\cdot9$ lbs. felspar would be necessary, this introducing at the same time

$$\frac{16\cdot3 \times 15\cdot9}{100} = 2\cdot59 \text{ lbs. } K_2O,$$

and

$$\frac{64\cdot8 \times 15\cdot9}{100} = 10\cdot3 \text{ lbs. } SiO_2.$$

2·59 lbs. K_2O may be taken as equivalent to 1·71 lbs. of soda, so that the deficiency of soda is now 1·21 lbs., and the excess silica 2·27 + 10·3 = 12·57 lbs. These may now be rectified by the addition to the formula of $\frac{1{\cdot}21 \times 100}{58{\cdot}5} = 2{\cdot}07$, or, say, 2 lbs. of soda ash, and the removal of 10½ lbs. of quartz. Consequently the recipe containing sodium silico-fluoride in place of cryolite must read :—

Borax,	20
Felspar,	46
Quartz,	19½
Soda,	7
Sod. nitrate,	3
Sod. silico-fluoride,	7
	102½

If china clay be employed instead of altering the felspar content, to introduce 2·9 lbs. alumina it is necessary to add $\frac{100 \times 2{\cdot}9}{39{\cdot}6} = 7{\cdot}3$ lbs. of clay. This brings in at the same time $\frac{7{\cdot}3 \times 46{\cdot}5}{100} = 3{\cdot}4$ lbs. of silica. The deficiency in soda, 2·92 lbs., is rectified by introducing $\frac{2{\cdot}92 \times 100}{58} = 5{\cdot}04$ lbs. soda ash, and $3{\cdot}4 + 2{\cdot}27 = 5{\cdot}67$ lbs. of quartz must be deducted. The formula, therefore, reads :—

20	Borax
7⅓	China clay
30	Felspar
24⅓	Quartz
10	Soda
3	Sodium nitrate
7	Sodium silico-fluoride
101⅔	

A typical recipe supplied by the manufacturers reads :—

Borax,	19·0
Clay,	12·5
Felspar,	47·2
Saltpetre,	2·3
Soda,	7·0
Sod. silico-fluoride,	12·0
	100·0

They further state that 1,000 lbs. cryolite may be replaced by 890 lbs. of sodium silicofluoride, 610 lbs. of clay, and 250 lbs. of soda; 560 lbs. of silica being withdrawn from the recipe.

THE PHYSICAL PROPERTIES OF ENAMELS, AND THEIR RELATIONSHIP TO CHEMICAL COMPOSITION.

Each and every ingredient introduced into the enamel, in addition to affecting it chemically, and physically so far as ease or difficulty of melting is concerned, influences it also as regards expansion, elasticity, durability, etc., and factors having been worked out for these properties, it is just as easy to calculate the increased expansion given to an enamel, say, by the addition of 5 lbs. of cryolite as it is to calculate the increased cost.

Expansion.—Vielhaber, Froelich, and other workers, have worked out schemes for reading the approximate melting point of an enamel, but the two methods tested showed differences of over 100° C. for the same enamel, and are, therefore, not reproduced here, because they are not yet sufficiently reliable to be of any value. The fusibility of an ingredient depends so enormously on the other ingredients present, that to generalise gives only a wide approximation. For the calculation of expansion, however, definite and useful figures are available. Practically all substances on heating increase in size, and the *coefficient of expansion of any material is the increase in length it undergoes when its temperature is raised through* 1° *C.* Thus, if a yard rod of any solid when heated from 0° C. to 1° C. increases in length by one-millionth of a yard, its coefficient of linear expansion is one-millionth, and to this value is usually given the symbol α. Thus α for such a material is 0·000001. If, instead of using a rod, a cube is taken, this will expand along its height, breadth, and thickness, and its expansion will be three times the linear. This value is called 3α, and for the material under consideration would be 0·000003. The cubic expansion (3α) for steel is 0·000000400, and for cast iron 0·000000310, and for average enamel in the neighbourhood of 0·000000300. To save the repetition of the series of 0's, these figures are usually expressed as 4×10^{-7}, or $3{\cdot}10 \times 10^{-7}$, or when the discussion is limited to enamels the $\times 10^{-7}$ is omitted, since it applies always, and is taken for granted. From the three values given it follows that the expansion of an enamel is in the neighbourhood of three-quarters that of the steel basis, and hence it is in a state of compression, whereas enamels for cast iron, being softer, are usually higher in expansion and may exceed the value for cast iron itself, which is considerably less than steel, and these differences may explain the faults due to crazing, etc., which are seldom seen in steel enamelling.

The classical work on the expansion of glasses has been done by Winkelmann and Schott, and later revised and adapted to enamels by Mayer and Hovas,* whose

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* *Sprechsaal*, xliv., p. 188.

values for the various ingredients are given in alphabetical order in Table VIII.

TABLE VIII.—COEFFICIENTS OF CUBICAL EXPANSION. (3α.) (All × 10^{-7}.)

MATERIAL.	$3a$.	MATERIAL.	$3a$.
Aluminium fluoride, .	4·4	Magnesium oxide, .	0·1
Aluminium oxide, .	5·0	Manganese oxide, .	2·2
Antimony oxide, .	3·6	Nickel oxide, . .	4·0
Arsenious oxide, .	2·0	Phosphoric oxide, .	2·0
Barium oxide, . .	3·0	Potassium oxide, .	8·5
Boric oxide, . .	0·1	Silica, . . .	0·8
Calcium fluoride, .	2·5	Sodium fluoride, .	7·4
Calcium oxide, . .	5·0	Sodium oxide, . .	10·0
Chromium oxide, .	5·1	Tin oxide, . .	2·0
Cobalt oxide, . .	4·4	Titanium oxide, .	4·1
Iron oxide, . .	4·0	Zinc oxide, . .	1·8
Lead oxide, . .	3·0	Zirconium oxide, .	2·1

From the table it is seen that sodium oxide heads the list with an expansion of 10·0, whilst boric oxide is bottom at 0·1, or one-hundredth the value for soda. The change in expansion by substituting soda for borax or boric acid in an enamel is, therefore, obviously great. The expansion of our sample enamel may now be given as an example. We cannot use the analysis as it stands, because it contains the ingredient fluorine, which is a gas, and, therefore, has no comparable expansion ; the analysis is, therefore, recast, showing the fluorine combined with sodium and fluorine.

OLD ANALYSIS.		NEW.	
Na_2O, . . .	14·5	Na_2O, . . .	10·8
K_2O, ...	5·9	NaF, . . .	5·7
Al_2O_3, . . .	9·5	K_2O, . . .	6·1
SiO_2, ...	56·8	Al_2O_3, . . .	7·7
B_2O_3, . . .	8·4	AlF_3, . . .	3·8
F_2, ...	4·9	SiO_2, . . .	57·1
	100·0	B_2O_3, . . .	8·8
			100·0

The expansions are now read from Table VIII. :—

Na_2O,	10·8	×	10·0	=	108·0
NaF,	5·7	×	7·4	=	42·2
K_2O,	6·1	×	8·5	=	51·9
Al_2O_3,	7·7	×	5·0	=	38·5
AlF_3,	3·8	×	4·4	=	16·7
SiO_2,	57·1	×	0·8	=	45·7
B_2O_3,	8·8	×	0·1	=	0·9
	100				303·9

which equals 3·039, compared with about 4·0 for steel. As a matter of fact, Mayer and Hovas determined the expansion of steel to be 4·05 when unenamelled, and 4·02 when enamelled. Originally it was considered advisable to have a ground coat enamel with an intermediate expansion between that of the steel and the cover coat, but the best modern practice suggests a cover coat with a greater expansion than that of the ground coat.

The figures given in Table VIII. are not to be accepted as the last word in expansion values, since the experimental work was limited, and empirical in character, and takes no cognisance of the fact that the expansion of the same material varies at different temperatures. Thus the increase in length of an iron rod when heated from 0° C. to 1° C. is not the same as from 300° C. to 301° C. The figures given, however, are extremely useful when used with discretion, and are widely employed in the glass industry.

Elasticity.—That the expansion coefficient is not the only physical property of importance is indicated by the foregoing remark that in the most durable enamels there is a big drop in expansion between the steel and the ground coat, and then a slight increase with the cover coats. Further, though it is possible to construct enamels with an expansion equal to that of steel, these do not produce such durable enamels as those in the neighbourhood of 75 per cent. of it. The successful enamels are elastic ones thinly applied, and Winkelmann and Schott's figures are given in the following Table IX., different values being given for lead and leadless enamels. The definition of Young's modulus of elasticity is, *the force required to stretch to double its length a sample of the substance of unit length and unit cross-section.* The values given in the table are expressed in kilogrammes per square millimetre.

TABLE IX.—COEFFICIENTS OF ELASTICITY.

MATERIAL.	Containing Lead.	Lead Free.
Aluminium fluoride, ...	80	92·5
Aluminium oxide, ...	70	100
Arsenious oxide, ...	40	40
Barium oxide, ...	30	70
Boric oxide, ...	25	60
Calcium fluoride, ...	...	50
Calcium oxide, ...	...	70
Lead oxide, ...	55	...
Magnesium oxide, ...	30	40
Phosphoric oxide, ...	70	...
Potassium oxide, ...	30	70
Silica, ...	70	70
Sodium fluoride, ...	50	71·5
Sodium oxide, ...	70	100
Zinc oxide, ...	...	100

Those materials with the low values are the more easily stretched, of which boric oxide is characteristic. Staley * gives a value of 15 to zinc oxide, presumably in a lead enamel, and consequently classes this with boric

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* *Enamelled Cast Iron Wares,* p. 119.

acid in this respect. The elasticity of the sample enamel is readily calculated :—

Na_2O, ...	$10\cdot8 \times 100$	$= 1080\cdot0$
NaF, ...	$5\cdot7 \times 71\cdot5$	$= 408\cdot0$
K_2O, ...	$6\cdot1 \times 70$	$= 427\cdot0$
Al_2O_3, ...	$7\cdot7 \times 150$	$= 1155\cdot0$
AlF_3, ...	$3\cdot8 \times 92\cdot5$	$= 352\cdot0$
SiO_2, ...	$57\cdot1 \times 70\cdot0$	$= 3997\cdot0$
B_2O_3	$8\cdot8 \times 60\cdot0$	$= 528\cdot0$
	100·0	7947·0

These figures again are not conclusive, but are extremely useful for comparison purposes.

TABLE X.—TENSILE STRENGTH.

MATERIAL.	Value.	MATERIAL.	Value.
Aluminium oxide, .	0·05	Magnesium oxide, .	0·01
Barium oxide, . .	0·05	Potassium oxide, .	0·01
Boric oxide, . .	0·07	Silica, . . .	0·09
Calcium oxide, . .	0·20	Sodium oxide, . .	0·02
Lead oxide, . .	0·03	Zinc oxide, . .	0·15

Tensile Strength.—Tensile strength is defined as the stretching force in kilogrammes required to rupture a rod of 1 square millimetre cross-section. Winkelmann and Schott's figures for this value are shown in Table X.

No reliable values have been obtained for the resistance of enamel or its ingredients to the opposite form of applied force—that is, one of compression—but it is doubtful if failure in enamels is ever due to a crushing force. Faults are far more commonly due to a weak resistance to tensile effects and poor elasticity.

Since a high tensile strength coupled with a low figure for elasticity is highly desirable, Staley* has divided the values of the former by the latter, the higher the quotient the more useful the material. Accepting his value of 15 for the tensile strength of zinc oxide, the values obtained are as in Table XI. :—

TABLE XI.—VALUES FOR $\frac{\text{Tensile Strength}}{\text{Coefficient of Elasticity}}$.

MATERIAL.	Value.	MATERIAL.	Value.
Aluminium oxide, .	0·0004	Magnesium oxide, .	0·0003
Barium oxide, . .	0·002	Potassium oxide, .	0·0003
Boric oxide, . .	0·003	Silica, . . .	0·001
Lead oxide, . .	0·0005	Sodium oxide, . .	0·003
Zinc oxide, 0·01			

Excepting zinc, his values differ from the above, his three highest fluxes being zinc oxide, boric oxide, and lead oxide, and he claims that these values bear out practical experience that enamels high in these oxides are more adaptable to variable conditions of the castings, heating, and working than those high in the usual alkaline fluxes.

Resistance to Mechanical Shock.—This depends, not so much upon the individual enamel ingredients as upon a perfect cohesion between the enamels themselves, and between the ground coat and the steel, although enamels high in lime and boric acid are notoriously weak. Thinness of the enamels is the best security against liability to chip easily. The same factors which govern resistance to mechanical shock apply also to

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* *Ibid.*

the case of sudden temperature change. The usual test for mechanical shock is some form of mechanical hammer which can be made to give a blow of known force at definite time intervals. When the enamel does fail, it should tear away the steel as well, and not merely flake off.

Resistance to Sudden Temperature Change.—This and the general durability depend largely on thin even coats of enamel, of good strength and elasticity. An enamel containing a high proportion of raw ingredients added to the mill on grinding is liable to be weak; another factor also causing weakening is the sudden cooling of the fused enamelled ware through draughts, etc. A test for an enamel's ability to stand temperature shocks is to submit it to the treatment it occasionally receives in the kitchen—namely, to boil water down to dryness in a vessel, and then whilst hot plunge it under the cold water tap. In order to standardise the conditions of this test, the best procedure is to boil some water in, say, a saucepan to dryness and to continue heating. The inside of the vessel is touched with paper, until this chars and stains the enamel. The paper is removed, and the heating continued until the stain just disappears, when the article is removed from the gas and filled with cold water. Should the enamel not chip, the test is repeated. A good enamel will withstand this treatment six times before chipping.

Resistance to Acids.—The term acid-resisting when applied to enamel means nothing unless the acid, its strength, and the conditions of the test are stated. No enamel will withstand all acids, for being largely composed of silica, it will completely disintegrate in hydrofluoric acid, and the silica will dissolve out. For special conditions such as those commonly met with in the chemical industries it is possible to construct an enamel with an excellent resistance to the strongest acids such as sulphuric and nitric, even at elevated temperatures, but this special resistance is obtained at the expense of other qualities which are not so necessary to this class of work, but vital to domestic ware. Again, there are varying degrees of the effect of the attack of acid on an enamelled surface. The first signs of the effect are slight irridescent stains on the surface, after which there is complete loss of gloss, then a pitted uneven surface, until finally the enamel completely disintegrates. It must be decided, in forming a standard, at which stage in this attack the limiting line will be drawn between satisfactory performance and unsatisfactory. In the kitchen the strongest acid likely to be encountered is the juice of the lemon or other bitter fruit. The strength of lemon juice is 7½ per cent. citric acid, but is not so potent in action as a pure citric acid solution of this strength, owing to the presence of the other ingredients in the lemon. Again, these juices are seldom used as they are, but generally well diluted with water. Any enamelled surface which would withstand boiling 10 per cent. citric or acetic acid for half an hour, with no serious loss of gloss, would certainly be satisfactory. It must be borne in mind that the greater the strength of the acid does not necessarily mean the greater the attack. Most acids are more potent at 10 to 20 per cent. strength than at 100 per cent.

An interesting and exceptional case recently came to hand of an enamelled bowl which had been used for making orange marmalade, and from which, after standing for 12 hours in contact with the orange juice, the enamel could be rubbed off. (It was claimed that no lemons had been used.) Orange juice contains but 1·35 per cent. acidity expressed as citric acid. The enamel was of a low melting nature and contained a small amount of lead. Its origin could not be traced.

Resistance to acid is achieved broadly by hardening the enamel. Increase of silica and alumina increase the resistance to acid, increase of soda and boric acid (except in a refractory enamel) reduce the resistance. Substitution of soda for boric acid favourably affects the resistance, and fluorides weaken the resistance. Prolonged melting has a favourable influence, as has also a minimum mill addition, both of which conditions tend to produce a more homogeneous enamel, which is better for the purpose.

The usual test is to boil rhubarb or some similar fruit in an enamelled vessel, strain off the fruit, and evaporate the juice to dryness, wash out and examine the surface.

The test can be very simply put on a more scientific basis, and standardised by the simple use of normal hydrochloric acid, and normal caustic soda, which can be easily obtained, together with a burette, which is a common article of laboratory equipment. The vessel is filled with the cold acid, and allowed to stand twelve hours, after which it is stirred ; 100 cubic centimetres are then withdrawn, and the soda run into it from the burette until the remaining acid has been neutralised (this is shown by a few drops of indicator, phenolphthalein). If x cubic centimetres of the soda are used, then the figure $100 - x$ is noted. For good acid-resisting enamels, this should be about 90, though 66 is usual.

A further test which has been devised is by means of a solution of narcotine hydrochloride, the strength being one in a thousand. Fifty cubic centimetres of this are taken and boiled in the vessel. If a cloud forms within ten minutes it is unsatisfactory. If the cloud slowly forms, and develops within 60 minutes, the ware is insufficiently good for medicinal purposes. If minute needles develop within 15 to 20 minutes, not increasing distinctly within an hour, the article is satisfactory. The article must be thoroughly cleaned with acetic acid, followed by water and alcohol, and then thoroughly dried.

Numerous papers have appeared, mainly in the *Journal of the American Ceramic Society*, dealing with all aspects of the relationship of physical properties to the chemical composition of enamels. A selection of these includes :—

"Tests on Ten White Enamels" (including Resistance to 20 per cent. Acetic Acid, Expansion, Contraction, Brittleness, Elasticity, and Adhesion). Landrum, *Trans. A. Cer. Soc.*, xiv., p. 489.

"Resistance to Various Strengths Acetic Acid." Landrum, *ibid.*, xiii., p. 494.

"Resistance of Glasses containing neither Lead nor Boric Acid to Citric Acid." Orton, *ibid.*, v., p. 305.

"Relative Action of Acids on Enamels." Poste, *J. A. Cer. Soc.*, vi., p. 689.

"Relationship of Chemical Composition to Acid Corrosion." Shaw, *ibid.*, xii., p. 463.

"Resistance to Concentrated Acid." Staley, *ibid.*, xiii., p. 499.

TABLE XII.

A Typical Page from a Recipe Book.

The most suitable means of keeping recipes is in a loose-leaf book, in alphabetical order, where they are readily traced. As an example, the same white formula may be given, the batch weights being altered to make the final analysis read to 100 per cent.

WHITE.

No. 54.

FOR FLAT WORK.

Quantity.	Material.	Cost per Lb.	Total Cost.	Yield.	Analysis.
Lbs.				Lbs.	Per Cent.
23	Borax, . .	At 2·14d.	49·2d.	12·0	Na_2O = 14·5
14	Cryolite, . .	At 4·39d.	61·5d.	14·5	K_2O = 5·9
34½	Felspar, . .	At 0·53d.	18·3d.	34·5	Al_2O_3 = 9·5
34½	Quartz, . .	At 0·43d.	14·8d.	34·5	SiO_2 = 56·8
5¾	Sod. Carbonate,	At 0·75d.	4·3d.	3·3	B_2O_3 = 8·4
3½	Sod. Nitrate, .	At 1·71d.	6·0d.	1·2	F_2 = 4·9
115¼			154·1d.	100·0	100

Cost per lb. = 1·54d.
+ Labour per lb. = 0·27d.
+ Coal per lb. = 0·16d.
1·97d.

Composition of Frit.

$$\begin{array}{lcl} 0{\cdot}787\ Na_2O & Al_2O_3 = 0{\cdot}313 & 3{\cdot}190\ SiO_2 \\ 0{\cdot}213\ K_2O & & 0{\cdot}404\ B_2O_3 \\ & & 0{\cdot}434\ F_2 \\ \hline 1{\cdot}000 & & 4{\cdot}028 \end{array}$$

Loss on melting = 13 per cent.
Expansion = 303·9
Elasticity = 7,947

Mill Batch.

Weight.	Material.	Cost per Lb.	Total Cost.	Yield.
100 lbs.	Frit, . .	At 1·54d.	154·0d.	100·0 lbs.
6 ,,	Wh. Clay, .	At 0·64d.	3·8d.	5·0 ,,
8 ,,	Tin Oxide, .	At 30·00d.	240·0d.	8·0 ,,
2½ ozs.	Mag. Ox., .	At 9·60d.	1·5d.	0·1 ,,
114 lbs.			399·3d.	113·1 lbs.

Cost per lb. = 3·53d. (dry weight).
Labour per lb. = 0·17d.
3·70d.

Water, 35 lbs.
Grind, 20 hrs.

Remarks.—

First tried August 1921.
Good gloss and opacity, but brittle.

CHAPTER VII.

THE PREPARATION OF THE ENAMEL.

THE preparation of the enamel will be considered under separate headings dealing with the three principal processes involved, (*a*) the mixing of the ingredients, (*b*) the melting of them to produce the frit, and (*c*) the grinding of this frit to produce an enamel in a suitable condition for application to the blank.

Mixing the Raw Materials.—The recipe for the enamel batch as indicated previously is merely a table containing six or a dozen items, together with the proportions of each to employ. Normally the utmost secrecy is observed regarding this possession, the recipes being carefully preserved from competitors who are quite likely using an identical or similar mixture. Such recipes in the possession of houses of repute have in the past attained appreciable value largely by virtue of the goodwill attached to them, and have changed hands for considerable sums of money. While these transactions were in vogue it was too much to hope that the system of secrecy would be dropped, but with the increasing number of people in possession of first-class enamelling formulæ, and the introduction into the industry of skilled men capable of creating perfectly satisfactory recipes, the trade in secret formulæ has been damaged, and the time may be nearly ripe for a pooling of knowledge and a more open discussion among enamellers of fundamentals, preserving to themselves what are really trade secrets only. An excellent comparison may be drawn between enamelling and cookery recipes, both yield different results in different hands, and in both cases good recipes in the hands of amateurs produce the most direful results. In short, the knowledge and experience of the operator are of far more importance than the piece of paper in front of him.

The processes about to be described require the closest scrutiny, and attention to cleanliness and all detail. The mixing and melting processes are in one sense two succeeding stages in the same operation, which is to produce a uniform homogeneous enamel, that will have the same properties throughout, and contain no patches of uncombined soda which will be readily dissolved off the final article, or lumps of infusible matter that will later break away. This result is impossible by mixing alone, but thorough mixing renders melting a simpler and more satisfactory process.

The first requirement is the reduction of the materials to a suitable mesh, and always maintaining this standard size of particle. This latter condition is important, because the chemical actions which take place in the subsequent melting process vary according to whether certain ingredients are coarse or fine. The refractory materials such as quartz are very much more difficult to incorporate in the molten batch if they are not finely ground. A similar explanation holds for the observation that such substances as felspar and cryolite cannot be replaced by their constituent parts. Felspar comprises potash, silica, and alumina, and it is a simple matter to mix these three in the same proportion as they exist in felspar. The action of the mixture, however, is quite different from the original felspar. However well the mixture may be made, the three components cannot be so intimately associated as they are in the mineral, and on melting the potash will liquefy first, and commence attacking the surrounding refractory material. Felspar, however, melts as a whole at the temperature of the melting furnace or slightly above.

The ideal enamelling plant would obtain the necessary minerals in rock from the mines, and possess the necessary grinding machinery for reduction to the desired mesh. This would be a means of controlling the enamelling materials right from the source. Few works contemplate such an installation, and depend upon suppliers for this part of the process. The importance of this stage cannot be exaggerated. Cheap grinding should be viewed with suspicion, and the finished material checked by passing through the appropriate sieve. The reduction of the bulk of a batch to pass a certain mesh is a simple matter compared with grinding the whole batch uniformly. The former will contain fine and coarse particles, and cannot be expected to behave uniformly in an enamel batch. The meshes generally desired by enamellers vary between 120 and 200. It is often necessary to further treat materials which have absorbed water either naturally or accidentally during transit. In the first category comes sodium nitrate, which invariably clots and requires running through a sieve prior to employment. Users of china clay, or *kaolin*, also need to sieve the product through the finest mesh which is commercially possible, otherwise, on melting, the particles of the difficultly fusible clay float on the surface of the batch and ball together, becoming quite infusible. This leads to flaws when the ground enamel is applied to the ware.

The materials must be dry before mixing or lumps will develop, and it is as well to run the final mixture quickly through a ¼-inch mesh, to catch pieces of string or other foreign matter accidentally included.

In view of the necessity for secrecy, a small but essential part of each batch is generally mixed by a manager or other confidential person, the bulk of the batch comprising the common ingredients being left to a workman to manipulate. In some works, in order to keep unauthorised persons still further in the dark, it is the practice to give each material a number, and refer to it by such and not by name, the suppliers of the materials being acquainted with the code, and supplying them with tallies bearing only the number. These efforts are usually negatived by the information supplied in railway consignment notes, etc., or by the peculiarity of bags for one particular material, whilst one case came to light of a consignment carefully labelled with a particular code number, being supplied in bags in which the firm's name, say The A.B.C. Borax Co., was woven. Further, with practice the workman becomes accustomed to the different materials, and recognises them at a glance, and the most satisfactory method of keeping this information within bounds is by selecting a reliable man initially and keeping him afterwards. An additional aid to secrecy is the introduction of the secret weighing machine, illustrated in Fig. 14. It may be set by a responsible person and then locked, after which the setting can neither be seen nor altered by the workman, who simply adds materials until a balance is obtained. Almost any number of ingredients may be handled, but these must always be taken in the same order, and naturally no ordinary scales where check weights could be made should be within reach.

The original method of mixing was turning the weighed materials over with a shovel on the ground, regarding mixing as complete when this had been done so many times, usually six. The many objections to this include its slowness, that it is dust-raising, and

Fig. 14.—Secret Weighing Machine (Avery).

depends upon the integrity of the workman. A distinct improvement is mechanical mixing, which is accomplished in rotating drum mills usually hexagonal in shape, running on a horizontal axis, and containing blades to help the mixing. Nothing extravagant is required, a wooden machine being quite suitable, and only a gentle rotation is required, a 3 to 6 H.P. motor supplying all the necessary power to mix a charge up to half a ton. The drums are generally worked in pairs, one being retained for white enamels. The charge will be determined by the capacity of the melting furnace, and 10 to 20 minutes' mixing is ample to produce the desired result.

The enamel-preparing department is the one part of the factory which it is desirable to build in more than one level, and here transport by gravity should be exploited to the full. A tall, three-storey building is the ideal, the uppermost being used as a store, supplied by a hoist outside, and an overhead runway inside. The materials are arranged so that the most used are the most conveniently situated, such materials as sodium nitrate, which take up water from the air, being kept in an air-tight container. The materials are delivered through chutes containing a rough sieve, to collect hard lumps, string, etc., to the floor below.

The down-coming materials are caught in a truck with a false bottom, placed on scales, and when the full batch has been weighed it is run over the chute, the bottom of the truck pulled out, and the batch allowed to fall through a second chute to the mixing mill below. After mixing, the batch is dropped through a finer sieve to another truck to await its turn for the furnace below. A rough sketch of the system is given in Fig. 15. Where this arrangement is too elaborate, a useful scheme for hand mixing is a series of boxes, of which the front does not quite reach the bottom. A sketch of this arrangement, looking end on, is given in Fig. 16. the

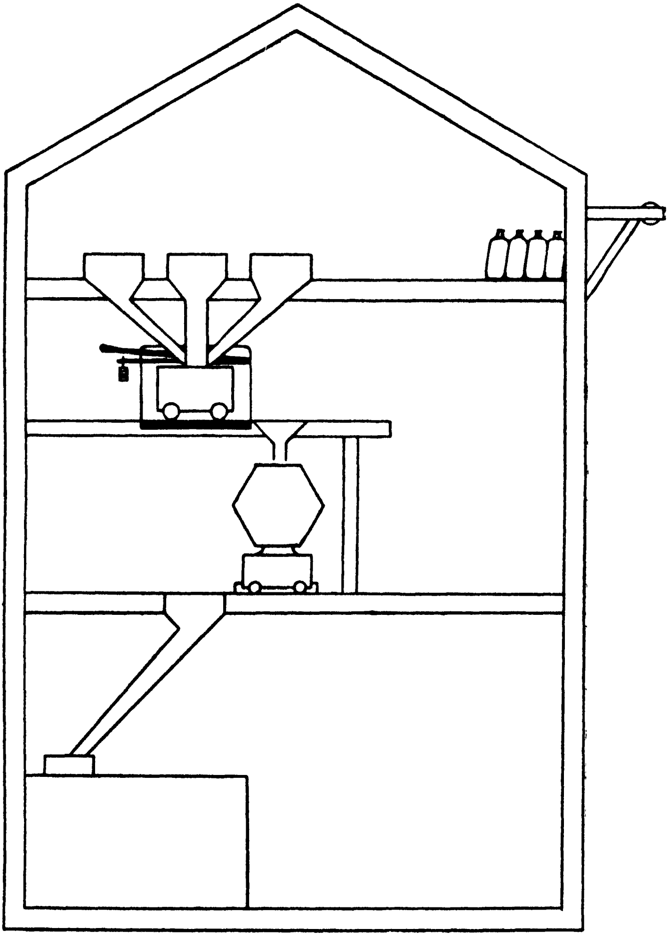

Fig. 15.—Elevation of Suggested Building for Enamel-Preparing Department.

idea being that as one shovelful of the material is removed another slides out and consequently the bulk of the material remains under cover, and waste and muddle are avoided.

Since, even with the enclosed drum mills, a certain amount of dust is inevitable, large airy rooms are desirable, with plain floors which are easily swept. Good ventilation is necessary, as owing to the proximity of the melting furnace the room is usually too warm when this is in action.

A certain amount of indecision exists as to the adoption of the English or metric system of weighing. This subject is only one small part of the Continental influence on the hollowware industry. As though our own units are not sufficiently numerous and bewildering, others are imported, with the result that an enamelled article is sometimes sold branded with a number, then in inches, centimetres, pints, litres, and number of cupfuls. In the particular instance of weighing raw materials, there seems to be little advantage to be gained by the introduction of kilogrammes. Materials are made up into 1-cwt. and 2-cwt. bags, with the exception of cryolite and other Continental supplies, and priced accordingly, and thus for stock-taking it is necessary to calculate in English measure. Certainly the metric system is much easier to manipulate, but against this is the necessity of having weighing machines specially graduated.

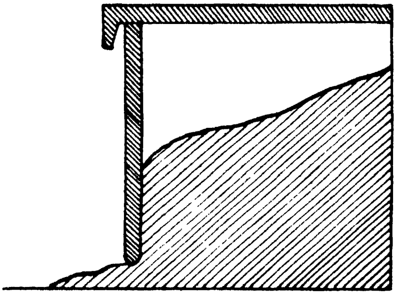

Fig. 16.—Bin for Raw Material.

Melting the Enamel.—Melting an enamel is analagous to glass making, and the allied industries which involve the alkali-alumina-silica system. They have this peculiarity, that their chemistry is that of the incomplete reaction, meaning that the products of the melt are not one or more definite compounds which are easily recognised and separated, but a uniform whole, and the composition of the melt depends on the time and temperature employed.

The process is in general carried out in reverberatory furnaces—that is, furnaces with a practically flat hearth and arched roof, heated by direct flames—though for special enamels, particularly enamels easily destroyed by the reducing action of the fuel, crucible furnaces similar to those employed in the glass industry have a limited use. The temperature desired is 1,200° to 1,300° C. Above this, melting is, of course, easier, but it is difficult to find suitable furnace lining material capable of withstanding the corrosion at these temperatures, and slight elevations aggravate the action appreciably.

The conditions and composition of enamels vary so enormously that it is impossible to give even a rough approximation of the output a furnace should produce without requiring relining, since, for example, a white enamel containing cryolite is more searching in attack than grey enamel, but 100 tons should be regarded as an absolute minimum. Sudden temperature changes are destructive to the brickwork, and for this reason it is advantageous to melt continuously for as long as possible—that is, throughout the twenty-four hours, and through week-ends, if necessary—rather than damp the furnaces down and reheat later. This means carrying larger stocks of chemicals and frits, and a consequent demand for storage space, but these disadvantages are more than counterbalanced.

The usual practice is to have two melting furnaces, one being reserved for white frits, though it may be necessary where the melters are continually in use to have two more as stand-byes whilst repairs are undertaken.

The fuel to be employed, and the consideration of fuel economy generally is left to Chapter X., but where coal is used, arrangements should permit of stoking from the side of the furnace remote from the enamel charging and tapping holes, and preferably outside the melting house altogether. The original furnaces fired by coal direct are always dirty, owing to small coal working over the bridge into the batch. The furnace hearth must have sufficient slope in it to allow the molten batch to drain off easily. The tapping hole may be at a point where the side wall of the furnace joins the bottom, or alternatively a hole in the bottom allowing a direct fall into a receptacle. The former requires some kind of channel, generally of cast iron, to carry the enamel clear of the furnace, and here some of the enamel solidifies however well the channel may be coated with clay to prevent sticking. This "stalk" should be put back with the next charge, and not used, as it is too hard to grind, and tends to clog the grinding mill. The direct fall method has the advantage of speeding up the running out, which in addition to saving time produces better enamel, because if this operation takes 20 to 30 minutes, both the first and last runnings cannot be correctly melted; either the first will be undermelted, or the last overmelted. Clay plugs are generally used for stopping the tapping hole, these do no harm to the enamel, except possibly hardening it a trifle. Iron crooks and other tools are necessary for thoroughly stirring the enamel, which is a necessary asset to good melting, but they should not be left in the hot enamel indiscriminately.

The actual size of the furnace bath varies enormously, since they are constructed to accommodate up to 2 tons. General practice is against the big batch, for though it may be cheaper per unit weight, the best quality enamel cannot be so obtained, largely owing to unequal heating. The time taken is largely determined by the height of the batch in the furnace, since the heat has to penetrate through from the top. Quick melting is, therefore, obtained by having a thin layer spread over a large area. A satisfactory thickness is 4 to 5 inches, and where a bath having an area 6 feet by 4 feet is employed a satisfactory charge is 500 to 600 lbs. Under these conditions a white batch should be melted in 75 to 90 minutes, a grey ground coat taking 20 minutes longer. A long slow melt tends to remove the fluorine with reduced opacity in consequence, whereas hasty melting may leave uncombined soda, which will weaken the enamel and destroy the gloss when the article comes in contact with water. Judgment in determining the completion of melting is helped by the peculiarity of one big bubble arising in the centre of the batch, a ripple passing to the extreme edge of the batch giving a similar effect to that following the dropping of a stone in a pool of water. When this happens melting is complete, and the furnace should be so constructed that this occurrence is readily visible. Facilities should also be provided to permit of the batch being thoroughly worked up with a crook throughout melting, since success is very largely dependent on constant stirring and any lumps of any unmelted material should be immediately dissipated. As soon as this bubble appears a white batch should be drawn, the ground coat being left a few minutes longer. Transparent frits for light colours may be carried still further, as in this case opacity is of no consideration, but gloss is of paramount importance.

Most practical men have a means of deciding when to draw a batch, the usual method being to draw a fine thread of the enamel by means of a rod and note the frequency of knots in it. Another test is to collect a cake in a shallow shovel from the molten batch, cool it, and examine the cross-section. The policy discussed in the final chapter of not working the factory through the night owing to supervision difficulties applies with much point to the melting operations, but where these are continued through the twenty-four hours, cakes and threads should be demanded of all batches, and examined in the morning, as a means of checking the working of the furnace overnight. The difficulty of continuous working is aggravated when it is necessary for the manager to be present when each batch is mixed to add his own portion to it, but against these difficulties must be set the distinct advantage to the life of the melter lining where the melting is continuous.

The simplest method of charging is through the roof by gravity, and the furnace must possess some means of cutting off the draught during this operation, otherwise the lighter particles get carried to the flues, melt, and collect there with consequent damage to the brickwork, and reduction of the size of the flue. This is particularly important where recuperator tubes exist; these being of small area, are easily choked. A continuous check on the melting furnace by means of a pyrometer is not possible, the simplest check being the clock.

As soon as the charge reaches the furnace, the edges of the heap begin to round off and the borax begins to melt. All the materials quickly lose the water and carbonic acid gas they may contain. One object of the melting process is to drive off all volatile matter, so that during the subsequent process, when the enamel is fused on to the steel surface, no further decomposition takes place. At the same time, the process is not carried beyond the point where a stable glass is formed, holding the opacifying materials in suspension. Over-melting means dissolving these with consequent loss in density, and the production of a glossy, almost transparent mass. As soon as the borax has melted it commences operations in two directions, the soda attacking any refractory material in its immediate vicinity, whilst the boric oxide content possesses the property of dissolving metallic oxides with the production of colours. It is an interesting education to repeat with enamelling materials a simple test commonly applied in chemical laboratories—namely, the "borax bead test." A loop is made in a piece of platinum wire by means of a pencil point or similar object the loop being about $\frac{1}{8}$ inch diameter, the wire is made red hot and dipped into borax, the adhering material is reheated until melted, and the process repeated until the loop is full of borax, forming a colourless, transparent glass-like bead. This molten bead, dipped into various compounds and reheated, may produce a coloured glass. The test is particularly obvious with a cobalt salt, a trace of this metal yielding a beautiful, deep blue bead. Other colours obtainable are :—

TABLE XIII.

	In Oxidising or Outside Flame.	In Reducing or Inside Flame.
Chromium Salts .	Green.	Green.
Copper, . .	Blue-green.	Red-Brown.
Iron, . . .	Yellow.	Bottle Green.
Manganese, . .	Amethyst.	Colourless.
Nickel, . .	Brown.	Grey.

The difference in the results according to the nature of the flame indicates the different results obtained in coloured enamels where insufficient nitrate is employed, or else none at all, to compensate for the flame in the melter, which for efficiency should be reducing in nature.

The borax is followed in melting by the nitrate, which quickly gives up its oxygen. The soda and cryolite melt next, the former losing its carbon dioxide and reverting to sodium oxide. The chemical reactions which now result are complicated by the conditions of the materials, their amount, and the temperature of the furnace. It may be taken as an axiom that the finer the grinding of the materials the quicker the melting process will become. This is simply the application of the chemical law that the speed of chemical action is proportional to the area of contact between the reacting substances, and the finer they are ground, the bigger the surface which is exposed. This is obvious in the case of a firebrick which may be dislodged from the wall of the furnace and becomes immersed in the enamel. After the melt, it is none the worse except that its edges are rounded off, whereas if the brick were powdered, it would have been dissolved in the batch. Intimate mixing and fine grinding, therefore, lead to quicker melting, saving of fuel and labour, and production of a better enamel.

The general practice is to splinter the enamel by running the molten stream into cold water. This produces a friable, granular frit which is easily reduced to powder. In fact, mechanical appliances have been introduced for appreciably reducing the size of the enamel crystals at the time of their formation in the water tank. It has been claimed that air cooling gives a more opaque enamel, which is in accordance with theory, since substances dissolved by the fluxes when molten may remain so on sudden cooling, whereas slow cooling would permit them to separate out, and thus cause opacity. At the same time, air-cooled frits must be more liable to devitrification, and the difficulties of reducing the material to powder must be appreciable. Water splintering, of course, produces huge volumes of steam, which should be drawn away by fans. Insufficient water may lead to an explosion, so running water should be employed, the hot water passing away at the top of the tank. Hence an adequate water supply, draining system, and sloping floors are necessities. The cleanest method of conducting this operation is in a white, glazed tile bath, a container having a perforated bottom being placed inside it to collect the frit. Where overhead runways exist this may then be transported on to the furnace flue to dry, after which it is good practice to weigh it into bags. A photograph in an American journal recently (*Ceramic Industry*) showed a continuous drying kiln which automatically discharged the frit into bags, dry, and in weighed quantities.

Checks on the quantity of frit obtained have invariably indicated that a yield approximating to the theoretical figure as calculated in Chapter VI. is obtained. In the case of white enamels, the frit usually possesses a bluish cast owing to iron impurities. Where a bottle-green tinge is present over-melting is usually the cause, a dirty colour resulting from lack of nitrate. Various materials are available for correcting the iron tinge in frits. Sodium selenite is used in the glass industry for the purpose, whilst enamellers generally employ a trace of cobalt oxide or manganese oxide, the former being more effective. The action of these materials is not chemical, simply depending on the compensation of colour, the blue of these oxides being complementary to the yellow of the iron. Where only one coat of white is applied over a ground coat, it must be borne in mind that this ground coat may affect the colour of the white, and usually is more than sufficient to neutralise any creaminess in the white.

Where it is the practice to store the frit loose in bins, it is worth while to graduate these to give a rough and ready idea of the quantity of frit in them.

The Wet Grinding of Enamels.—From this stage onwards the utmost regard must be paid to cleanliness. Hitherto any extraneous matter has had to pass through the melting furnace which may have either eliminated or lessened its effect; but henceforth all dirt and dust entering the enamel becomes very obvious on the final article. For this reason wooden containers are not advisable for storing frits, any splinter of wood most certainly disfiguring the enamel. The cleanest-looking material for storage bins is the white glazed tile, though naturally expensive. Failing this, concrete is a good substitute. Where bins are employed, sloping bottom with drain connections are advisable for removing any remaining moisture.

The whole layout of the enamel-preparing department should aim at cleanliness and simplicity. A clean appearance is produced by having white, tiled walls for the first 3 or 4 feet, with whitewash above. Provision should be made in the design for :—

(*a*) Light, airy, and dust-proof rooms; capable of warmth during winter.

(*b*) Accommodation for the stored frit, chemicals for mill addition, and wet enamel.

(*c*) Means of transporting enamel to enamelling department.

(*d*) Stove for boiling water for dissolving borax for ground coat enamels, and for boiling clay in water.

(*e*) Ample water facilities, sloping floors, and hose for washing down.
(*f*) Arrangements for sieving the enamel.
(*g*) Weighing machines.
(*h*) Means of illuminating the interiors of the grinding mills for inspection purposes.
(*i*) Storage for spanners and other necessary tools.
(*j*) Motors for driving mills supported on brackets and not on floor level.
(*k*) Means for locking up the building to protect the valuable tin oxide and to exclude unauthorised persons.

The old method of grinding enamels in the open pans has been superseded by the more modern process of grinding in a totally enclosed mill, usually a drum mill supported on a horizontal axis. Various means of grinding exist; the systems most adaptable to enamelling being the ball, stone, or tube mills, and the use of flint stones is generally the one selected. In this case grinding takes place by a mixture of crushing and abrasion.

Mills are generally mounted in line, frequently from the one shafting which is driven by the one electric motor. Modern practice is to provide each mill with its own motor, though in either case the motor should be overhead. Belt drive is advocated for smaller mills, gear drive for the larger, the dividing line being in the neighbourhood of 4 feet diameter mills. Most efficient grinding is obtained where the outside of the drum runs 400 feet per minute, which in the case of a 4 feet 6-inch mill is 28 revolutions per minute. A recent improvement is the mounting of mills on ball bearings, the increased cost being more than compensated for by the longer life obtained.

The object of grinding is to produce a uniform-sized particle; rough grinding is far simpler and cheaper, but producing, as it does, a variety of sizes from the roughest to the finest, is useless for the present purpose. There is only one test for the degree of grinding—that is, the passing of the enamel through a sieve or similar apparatus of the desired mesh, and its inability to pass the next fine mesh. 40 mesh is used for ground coats and 60 mesh for white. Rough control is obtained by timing the run of the mill, but two mills of the same capacity coupled to the same shafting will vary owing to differences in the belt slip, and the degree to which the mill lining is worn. The first fault is eliminated by having a counter on the axle and considering revolutions instead of time, but it does not eliminate the second difficulty.

The material of the mill lining is highly important. It obviously must be harder than the enamel, and also must contain nothing injurious to it. The choice is practically restricted to porcelain and the newer quartz, the difficulty about the latter being the cutting of it to fit the drum, thus rendering it more expensive, and opinions differ as to whether the increased cost is compensated by the increased life obtained. Certainly the porcelain is more easily fitted, lining with quartz being work for a specialist. It is essential that the inner surface be smooth and uniform, for the wearing effect will concentrate at any weak spot, and the lining soon be worn through there, whereas the remainder may be quite sound. The points most susceptible of attack are near the running-out hole, and the development of a bad spot at one particular point here may be prevented or delayed by twisting the driving belt and reversing the direction of revolution of the mill. This will cause the " throw " of the stones to attack another point.

American manufacturers are experimenting with a special rubber lining, for which strong claims of efficiency are made.

The best stones to employ are selected white flints, those from the beaches of northern France being preferred. The weight of stones used for efficient grinding should equal or slightly exceed the weight of frit being loaded, and the whole mill should be no more than five-eighths full. If the flocculating agents are not added at the commencement of grinding, but are delayed until about an hour before its completion, grinding will be quicker owing to the liquid being thinner. The same effect is produced if more than enough water is added initially, the enamel being allowed to stand after grinding and excess water decanted off.

The general rule to be applied to the addition of ingredients to the frit on grinding is that they should be reduced to an absolute minimum. It is essential to add clay at this stage, since heating in the melting furnace would destroy its ability to hold the enamel in suspension. The other mill additions include the pigments for coloured enamels, and tin oxide and its substitutes for white enamels. Usually there is no choice as to quality of the water to be added ; it has to be taken as it comes, though the purity of it, like every other ingredient, plays its part in determining the quality of the final enamel, and it must not be forgotten that about 40 per cent. of water is used, and even if this does evaporate, the residue from it remains.

The usual impurities in tap water are the bicarbonates of calcium and magnesium, together with their chlorides, and smaller quantities of the sulphates. The bicarbonates change to carbonates on boiling the water, and are thus deposited. Hence when the practice is followed of boiling the clay with water before use, the carbonates may be separated at the same time as impurities in the clay. Should the water be very hard (*i.e.*, contain undue proportions of these salts), the enamel will lose gloss. Enamels made with pure water in addition to having a better finish were found to be firmer in the " biscuit " state (*i.e.*, when dry, before firing), and were thus easier to handle. Where excessive amounts of hardness are suspected the tests for chloride and sulphate given under borax, Chapter III., p. 32, should be applied. It is, of course, possible to collect the rain water from the roofs and employ it for enamel-making, but, in view of the fact that an enamelling factory is usually well provided with chimney stacks, soot and other deposits will probably be present in plenty, and consequently no advantage from such water gained.

The size of mill selected will depend entirely on the output of enamel required. The largest which is practicable should be employed for economy, since it is almost as quick to charge the largest as the smallest mill, and more uniform results are obtained by using a big mill once in place of several charges from a small mill.

Bearing in mind the limits of capacity given above, a 4-foot 6-inch mill accommodates a charge of half a ton conveniently, together with the same weight of stones. The best results are obtained by loading a mill initially with only about one-third the weight of frit, together with the clay, colour oxide, and all the water, the remaining two-thirds of frit being added some hours later. Such a practice, however, is heavy on the mill lining. For safety's sake, a sample should be taken from each mill, and an article dipped therein and fired before the full contents are drawn.

Where it is desired to measure accurately the addition of the water to the frit, the simplest method is from an overhead tank fitted with a gauge which may be read at ground level. Where, however, the enamel is stored before use, excess water may be used, which facilitates grinding, and it may be removed from the storage tanks until the enamel is of the desired consistency. The enamel should certainly be stored from seven to fourteen days before use. This renders it more workable, and that without any tendency to waviness, due to uneven coating, necessitating less salt addition, and producing a richer and more lustrous finish. Two methods are available, storage tanks, containing the contents of a definite number of mills, or smaller units, such as pails, kept in rows on shelves. The advantage of the latter is that in case of accidental contamination the quantity of enamel wasted is small. Pails, however, soon become damaged, and lose their appearance. Further, they make excellent receptacles for dust, and dust is always very obvious in the fired enamels, either as specks or holes. The simplest process is a galvanised tank, which can be run under the grinding mill, filled through a sieve, kept the necessary number of days, and then wheeled to the enamelling department. Wet enamel is sometimes run over an electromagnet for the removal of iron specks, though it does not remove iron compounds, of course, which are more of an annoyance to enamellers than metallic iron. Any system of gravity supply through pipes to the enamelling benches is impracticable, owing to the distance to be covered, resulting in settling and clogging of the pipes.

Dried Enamel.—This product, usually referred to as "waste," is inevitable in enamelling, though the latter name is rather a misnomer, since the product is distinctly valuable, and a short experience with it will indicate that it is well worth taking care of. All forms of waste, such as that made by the splashings from the workpeople applying the enamels, their finger bowls, from the spraying booths and all washings (except floor washings, of course), should be collected and deposited in settling tanks. When the quantities are appreciable, it may be graded into two classes, the better being collected separately according to colour and used again directly as a mill charge, the other being refritted, which is the safer plan. On settling, the watery layers should be run off through a series of settling tanks until when the drain is reached nothing but water and the finer clay particles pass away. The sludge is collected and dried by the waste heat from furnaces. Where it is refritted, 10 per cent. borax and 5 per cent. nitrate should be mixed with it. White waste so produced is useful for making the lighter coloured enamels, miscellaneous waste being used for dark colours. As a very rough approximation, 5 per cent. waste on the total enamel made is a reasonable proportion, though it varies enormously with different conditions. Spraying produces a large proportion of waste, a condition which also applies where small quantities of special colours are required, such as in sign plates.

CHAPTER VIII.

THE GROUND COAT ENAMEL.

THE bulk of enamelled ware has three coats of enamel, involving three fires, whilst decorated ware, and hearth and sign plates may have more. Best quality white ware has two white coats over a ground coat, whilst for cheaper ware one white covering may be eliminated. Since it is impossible to apply a tin oxide enamel direct to steel, and almost equally difficult to obtain a white enamel free from tin oxide, which can be applied to and retained by the steel, a distinct ground coat has to be employed. It is this dark-coloured foundation for a white article which usually first excites the curiosity of the layman on making his acquaintance with the enamelling process, and which appears at first sight to be an extraordinary procedure. Unfortunately, all cobalt compounds are coloured, and so far cobalt has not been eliminated from the list of necessary enamelling materials. The word indispensable can scarcely be applied to cobalt for ground coat use any longer, as durable ground coats are produced without its use, though its chief rival, nickel, also colours the enamel. The so-called white-grey ground coats—that is, those containing no coloured oxide at all—are considered a little later. Tin oxide has been described as the enameller's *vade mecum*, but cobalt has been his constant companion throughout the ages, primarily for use as a blue pigment, but later as an indispensable ingredient of ground coats for sheet steel. In addition to possessing the undesirable quality of colouring the ground coat, cobalt compounds share the chief objection to tin oxide —namely, high price—cobalt oxide being the most expensive raw material employed, though fortunately the quantity necessary is of modest dimensions.

A theory often advanced for explaining the peculiar adhering qualities of cobalt is that its coefficient of expansion agrees closely with that of iron. This is disproved by the extremely small proportion used, often less than ¼ per cent. Were this quantity multiplied a hundred fold it would not materially affect the expansion of the final enamel. The theory is further negatived by making ground coats of equal expansion to steel, but containing no cobalt, when the original good adherence cannot be reproduced. A more reasonable explanation advanced is based on the general chemical similarity of iron, nickel, and cobalt. The micro-photographs of the piece of steel covered with a cobalt ground coat show how the latter has worked below the surface of the metal, owing to its spongy nature following pickling, after which some chemical action between the iron and the cobalt probably results during the fusing process, when the iron may become oxidised, and produce a double compound of iron and cobalt. This explanation applies equally well to nickel, which almost invariably substitutes cobalt either partially or entirely. Since nickel produces a dark enamel, the economy is derived solely from the difference in price of the two oxides. Consequently, as far as the process is concerned, cobalt and nickel ground coats belong to the one class, in distinction from the white-grey ground coats. A borderline case is given by ground coats containing iron oxide as the only coloured ingredient. Chemically they belong to the cobalt, nickel class, though the colour of the final enamel produced is only slightly deeper than the white-grey enamels.

White-Grey Ground Coats.—Considerable progress has been made with these last-named ground coats, and it is possible by a careful blending of the materials usually reserved for white enamels to produce an enamel which has an expansion and other physical qualities similar to the usual enamels, and a good adherence to steel. Such an enamel usually contains opacifying media, such as antimony oxide or zirconia, though tin oxide cannot be introduced. These oxides are generally fritted with the other ingredients, the loss in opacity being more than compensated by strength of the enamel. A typical example reads :—

Antimony oxide,	3·6	per cent.
Borax,	31·8	,,
Calcium carbonate,	1·7	,,
Clay, white,	2·2	,,
Cryolite,	7·2	,,
Felspar,	19·7	,,
Fluorspar,	1·8	,,
Potassium nitrate,	3·6	,,
Sand,	23·3	,,
Soda,	5·1	,,
	100·0	per cent.

This requires thorough melting, and is milled in the usual manner with borax and clay ; it must be applied thinly. Firing requires extreme care, there not being the margin that there is with cobalt ground coats, it being extremely easy to overfire, with consequent blistering. The above frit has an expansion of 290, and costs slightly more than the normal ground coat, hence there is no direct saving here. The economy occurs in only one further coat of white enamel being necessary. In fact, more may not be applied, as the enamel then becomes too liable to chip. Such an enamel has a good durability, and may prove serviceable for simple shapes of cheap quality, but will fail on complicated patterns, and cannot be recommended for first quality ware. Most people who experiment with this type of enamel return eventually to the coloured ground coat of universal application.

Falling into a different category is the class of ware known as granite, silica, marbled, speckled or mottled ware, which has but one coat of enamel altogether, this being a cobalt ground coat of a pleasing shade. Some simple form of decoration is applied before firing, such as speckling with another colour, or mottling may be produced in the enamel itself by having a low clay content and adding a solution of cobalt and nickel sulphates, though the best mottles are produced in a second coat over a standard ground coat. The outstanding advantage of this one-coat ware is its extreme durability owing to the thinness of the enamel, and it will stand the buffeting of household use without easily chipping, and is particularly adapted to such domestic articles as bowls and basins. This ware is a feature of the American market, but is unpopular in this country, the demand being always for white ware. Consequently, its introduction here depends, not on the enameller, but on the ability of his salesman to convince the housewife that appearance should be sacrificed for utility.

For a durable enamel, the one of highest possible melting point is the best, and this maximum temperature is usually determined by that at which the steel blank will soften and lose its shape, which, of course, is dependent on the gauge employed, and will usually vary for different classes of work in the same factory. Its hardness may be influenced further by the cover which is to follow it; in general, a drop of 50° C. in the softening point for each succeeding coat of enamel being required. Further, a good ground coat requires to have a long range of temperature for softening, while the cover coat should melt quickly. To maintain a series of ground coat enamels to meet all contingencies is usually inconvenient, and one or possibly two different frits should suffice. The hardness is then modified by the addition of finely-ground quartz or flint at the mill. Cheap enamels may be made from soft frits run through the melting furnace easily, and then hardened by the addition of 20 per cent. quartz at the mill, even 40 per cent. being used in continental practice. This obviously weakens the enamel, and where this is not desired, it may be useful to possess two ground coats, the one hard and the other soft, blending them in any required proportion. In a hollowware factory the hard one may be used by itself for cooking utensils, and the softer one for articles not required to stand heat treatment.

From the selection of raw materials mentioned in Chapter III., the ingredients for making ground coats are generally drawn from borax, calcium carbonate, cobalt oxide, felspar, flint, fluorspar, iron oxide, manganese dioxide, nickel oxide, potassium and sodium carbonate, potassium and sodium nitrate, quartz, and sand.

An example of hard and soft ground coats reads :—

	Hard.	Soft.
Borax, . . .	31·8 per cent.	33·8 per cent.
Cobalt oxide, . .	0·3 „	0·3 „
Felspar, . . .	29·1 „	44·1 „
Fluorspar, . . .	4·1 „	9·0 „
Manganese dioxide, .	0·1 „	0·1 „
Potassium nitrate, .	5·5 „	3·1 „
Quartz, . . .	20·1 „	5·5 „
Soda, . . .	9·0 „	4·1 „
	100·0 per cent.	100·0 per cent.

An example of a universal frit for ground coat reads :—

Borax,	28·5 per cent.
Cobalt oxide,	0·35 ,,
Felspar,	31·2 ,,
Flint,	20·0 ,,
Fluorspar,	6·0 ,,
Manganese dioxide,	0·95 ,,
Soda,	9·0 ,,
Sodium nitrate,	4·0 ,,
	100·0 per cent.

It will be seen that felspar forms the main constituent, always exceeding the quartz, except in the case of particularly hard enamels. Next in order of quantity comes borax, which may occasionally exceed the felspar. The three items mentioned approach 90 per cent. of the whole, the remainder being made up of soda, fluorspar, and the colour oxides of cobalt, nickel, and manganese.

Manganese dioxide produces a very dark enamel, whilst it is usually desirable to have as light a ground coat as possible.

The liquid enamel requires to be thin, containing approximately 40 per cent. of water (calculated on the weight of frit). Six per cent. of a good quality clay is sufficient, and apart from the possible addition of quartz, the only other requirement is a salt for flocculating the clay, and the best and only one necessary is borax. This should be added immediately before use and curtailed to a minimum. The liquid enamel, which is ground rough—that is, just to pass a 40-mesh sieve—should be kept in the mill if possible for a few days to mature, and the borax which has been previously dissolved in boiling water added about an hour before the enamel is required, and the whole thoroughly mixed. Temperature makes an enormous difference to the solubility of borax, as this substance possesses the peculiarity of being but slightly soluble in cold water (1·6 per cent. at 10° C.), and very soluble in hot water (200 per cent. at 100° C.). It is, therefore, obvious that a lowering of a few degrees in temperature may make the difference between a solution of borax, and water containing a deposit of borax crystals. These latter, if present in the enamel, fly off during the fusing process, leaving spots which are a consequent source of trouble. It is generally a winter-time fault, and it is good practice to reduce borax and increase clay during this season. This emphasizes the necessity of keeping enamels in a warm place. The maximum addition of borax should be less than 1½ per cent.

A good test for determining whether or not a piece of iron or steel is completely covered with enamel is to immerse it in a solution of copper sulphate, when red-brown copper will be deposited on any exposed portions of iron.

Of the many difficult tasks confronting the enameller, the most difficult is the production of a satisfactory ground coat, and when this is achieved he will, if he is wise, leave well alone. In the event of faults arising during enamelling, he should try all other expedients before tampering with the ground coat. The result of changes here are often not seen for months, when customers' complaints begin to appear, and one flood of such complaints is usually sufficient to impress upon him the motto, *festina lente*, where ground coat charges are concerned.

The actual application of the enamel to the article is achieved by one of five methods, the simplest, painting on with a brush, being reserved for flat work. The principal method for hollowware has been referred to here as dipping, though in various works it is known alternatively as swilling or slushing. The remaining methods are draining, spraying, and dusting.

The aim being to produce the covering of the article with as uniform a thin coating as possible, the method selected depends entirely on the weight and shape of the article. It must be appreciated at the outset that success depends entirely on the quality of the labour. There appears to be no possibility of covering anything but the simplest shapes by an automatic process.

Dipping.—The great majority of pieces are covered by this means, which involves the immersion of the article in the liquid enamel by the operator, and then by a number of deft movements the surplus enamel is removed and a uniform coating obtained. Considerable training is required to attain perfection in this art, and it is best achieved by concentrating one worker on one particular article. Some obtain the best result by holding the article in the hands, others by using tongs, but, as a generalisation, it may be asserted that tongs should be employed wherever possible. Some people, however ambitious or persevering, can never learn to produce the desired result, as success depends so largely upon supple wrists. The most common fault is the concentration of the enamel in the centre of the article with a consequent thinning at the edges, the effect being readily obvious after fusing. A further limitation in the choice of labour is due to the liability of some people to dermatitis (skin disease) through association with enamel. The enamel is not necessarily to blame for this, but more likely the sensitivity of the skin, the same people being unable to maintain their hands in soda or strong soap solutions. Any cases which have come to the writer's notice have all been associated with the coloured enamels containing iron and chromium compounds—that is, brown, green, and black enamels. Not one case has occurred with ground coat enamels which normally contain the most free soda. The explanation regarding the colours appears to be the difficulty of removing iron stains from the hands, and when cracks are caused by the soda, the iron gets into these, and then any neglect in the matter of thorough washing leads to trouble.

Draining.—This is carried out with a much thinner enamel, the article being simply immersed and then allowed to drain, assistance being given by rocking the piece. It is a method applicable only to flat work, being seldom satisfactory for anything else.

Dusting.—This is the application of enamel as a dry powder, and is confined to cast iron, being obsolete as far as sheet steel is concerned. It possesses the advantage of requiring no mill additions to the frit, which is a distinct advantage when resistance to acid is a primary consideration. See Chapter XI.

Spraying.—This is considered in the next chapter under cover coats. The necessity of obtaining a uniform coating being such an essential, keen supervision is of first-rate importance, particularly where the generally applied system of piece-work basis of remuneration exists. It is useful to sectionalise the department into groups of six workers or more under a foreman or forewoman, and endeavour to create a spirit of competition between the sections. The pots of enamels require sieving at least every 24 hours, and this may be achieved conveniently overnight, the foreman examining each one and setting up the enamel where necessary every morning. The articles, clean and free from dents, should be marked for each dipper, so that faults which are discernable only after firing may be brought home to the guilty party. A good organisation should permit of a dipper doing nothing else but dipping, all carrying and repairing being done by other labour. The actual method of setting the work to dry depends entirely on its nature, the general rule of marking the work as little as possible being the chief consideration.

Drying.—Ground coat ware must be dried as soon as possible, for although all enamels are slightly alkaline, and the metal surface has a film of soda on it, rust spots easily develop, even with the quickest drying, and in this case a little soda solution should be added to the enamel, though obviously of insufficient proportions to cause trouble. The waste heat from the fusing furnace flues is generally used for drying, though it may be necessary in winter to have additional sources of heat, such as circulating hot water, one novel idea being the actual construction of the drying racks with pipes carrying the water. Any access to external draughts should be prevented, and the whole drying area maintained like a hot-house. There should be no delay at this stage for fusing, each day's dipping output being fired within the succeeding 24 hours, and in a works handling a variety of ware it requires intelligent organisation to judge and arrange these matters. A further advantage of quick progress is the smaller space required for drying and similar storage centres. The obvious place to have the drying racks is between the dipper and the furnace, to minimise handling and transport. Experiments with the dryer conveyor similar to that mentioned in the pickling department, indicate that it is limited to cast and similar heavy ware, a machine of sufficient delicacy for handling light domestic ware not having appeared so far. A further difficulty is that in general the furnaces work more hours than the dippers, the latter in 8½ hours being required to keep the furnaces going for 24 hours as a rule. Hence stacking is necessary, which may be combined with examination. Another attempt at mass movement is the portable rack containing one or two hundred pieces, which may be picked up on a rubber-tyred, ball-bearing truck and thus transported. Imperfections in the floor soon upset this method, and a better process is suspension from an overhead runway. Where this is not available, girls of 14 to 16 years of age carry racks bearing a few pieces, and it is from this class that the most intelligent are selected for training as dippers.

Fusing the Ground Coat.—Enamelled ware is practically always fused in a muffle type of furnace, and the first requirement is a uniform heat from front to back, excepting the first few inches inside the door, which are bound to be cooler, owing to contact with the outside air. A further requirement is that the muffle be absolutely sealed and allow none of the flue gases to enter through cracks. These, if charged with sulphur, destroy the finish, and, further, the sudden heat may burn off the enamel at one point. As in drying, the actual methods of drying the ware are diverse, the same general principle applying of marking the ware as little as possible, together with stability during loading and unloading. Skilful design of the fire bars is necessary to ensure economy of space together with a uniform heating, or alternatively greater heat in the thickened portions. These bars should hold the ware well above the floor of the muffle, and yet contain no unnecessary iron work owing to heat absorption and the formation of scale. The actual contact between the holder and the article is usually a point—namely, a pointed spike—and the size of this is less important in ground coats than later on, but must not be too large, or the enamel will be removed to such an extent that subsequent coats will peel away from the spot. The equipment utilised to the greatest extent for ground coat fusing is plain bars having a fine edge for use with articles with a foot, and notched bars for flat articles. Except for large articles, no straightening of the article should be necessary after fusing the ground coat. For most economical working uniform loads should be fused, with the exception that small articles may be fired at the door end of the load. This proceeding obviates the necessity of continually changing the bars.

The system should permit of an examination of the ware to be made prior to fusing, and the simplest method of accomplishing this is by having one load spread out on a table while the previous one is fusing. The temperature of fusing requires to be in the neighbourhood of 900° to 950° C. ; above this the metal base will not stand, and enamels fusing below this temperature will be soft, and lack durability. The time of fusing is naturally very variable. Anything less than three minutes cannot be regarded as satisfactory, even for the lightest of gauges, whilst five minutes is more reasonable, and for the heavier sheets, up to ten minutes may be necessary. Thus, with facilities for quick loading, eight loads per hour is a fair average. The quick return of the load to the furnace is essential for satisfactory working, otherwise the bars get cold, and the ware near them has no chance to fuse properly. After fusing the articles should have a glossy surface, and in the case of cobalt ground coats correctly fired should have just turned from blue to grey-brown in colour. Here, again, one is in the hands of the fuser to a large extent. It is possible to regulate the temperature of the muffle, but the man's judgment determines when the load is to be withdrawn from the furnace. The fuser's occupation is one calling for care and judgment, though the special skill and experience of the dipper are not required.

Naturally, where there is more than one furnace, one will be reserved especially for grey fusing, and maintained at a suitable temperature, otherwise it has to be continually raised and lowered for grey and finished ware, in which case it is usual to fuse the ground coat work at nights.

The keenest of examinations is now required, since holes of pin-head dimensions produce appreciable areas of uncovered enamel in the finished stage. Any article bearing cracks, blisters, and similar defects must be rejected, and an intelligent decision made as to whether the articles are beyond redemption, simply require re-firing, or re-dipping and re-firing, or repairing, re-dipping, and re-firing. In addition to possessing a uniform finish, ground coat ware should possess great durability and toughness, capable of being dropped 4 feet on to a hard floor without damage, and an equally good resistance to sudden temperature change.

CHAPTER IX.

COVER COATS—WHITE AND COLOUR.

THE greater part of domestic ware is required to be in white finish, and a decision has to be made whether this is to be achieved with one or two coats of enamel over the ground coat. For high quality work the question is readily answered, an insufficient covering power being obtainable with one coat. For cheaper quality it is largely a question of economics, the pros and cons of the one-coat process roughly being :—

(*a*) Quicker progress, hence less overhead expenditure, with a bigger output and less space, labour, and fuel required, the proportion being roughly three to two.

(*b*) Where a second coat would be given a new article now takes its place.

(*c*) Less enamel is used, though it is more expensive, and more is required than for an ordinary coat.

(*d*) One coat ware is generally made for unassorted quality, hence there is no delay, and less unproductive charges for grading.

(*e*) There may be no mistakes made in enamelling. Minor faults in the ground coat which cover with two coats of white, may remain obvious in one coat ware.

(*f*) A higher proportion of rejects is inevitable. Can these be disposed of profitably ?

(*g*) If these rejects are re-dipped and then sold alongside one coat finish the distinction is unfavourably prominent, thus leading to complaints.

(*h*) Very skilful dipping is required, and more careful handling generally.

(*i*) A compromise has to be made between opacity and gloss, whereas with two coats either can perform its allotted task.

(*j*) When two coats are applied, the first provides a good training ground for young dippers.

(*k*) The same price cannot be obtained for both qualities. One coat work forms a market on its own, all buyers being sufficiently educated and keen to distinguish the two.

(*l*) It is a difficult enough task to produce a good white enamelled article with two coats. Is it not expecting too much to attempt it in one ?

First Coat White.—When two coats of white are decided upon, this coating becomes analagous to the painter's " primer," to be followed by a glossy " finish " covering—*i.e.*, the special function of this coat is to produce an opaque layer to hide the ground coat. Attempts have been made to carry this intention to the extreme, sacrificing gloss to produce a dull opaque enamel containing a maximum of the cheap opacifiers, fluorides and clay, relying upon the subsequent coat to produce the required gloss. The attempt fails because it necessitates unbalanced enamels, and sacrifices durability. Experience indicates the necessity of making both enamels the same fundamentally, and producing the necessary differences by less drastic changes.

The materials available for making the first coat frit include all those in Chapter III., excluding the colour oxides. Economies are sometimes effected at this stage by the partial substitution of sand for quartz, sodium nitrate for the potassium, by the use of a cheaper grade of felspar, the introduction of ground glass, and, provided it has been rigorously preserved from contamination, the white waste from the dipping pots and spraying booths. One disadvantage of the latter is that it renders calculation as to hardness, fusibility, and other physical properties either difficult or impossible, and the enamel can be judged only after prolonged use in practice. Sand is slower in fusing than quartz, and whilst this melting point is being attained, the opacifiers are being destroyed. It is generally agreed that expansion and fineness of grinding should steadily increase from ground coat to finish coat, whilst melting point must steadily drop.

The borax content should not exceed 30 per cent., cryolite may be present to the maximum practical limit, and normally the felspar content should exceed that of the quartz. Additional alumina may be obtained from a small inclusion of china clay, a typical recipe reading :—

1*st Coat—White.*

Borax,	27·5	per cent.
China clay,	2·9	,,
Cryolite,	13·9	,,
Felspar,	27·5	,,
Quartz,	19·3	,,
Soda,	5·7	,,
Sodium nitrate,	3·2	,,
	100·0	,,

Mill additions to 100 lbs. Frit.

White clay,	7 lbs.
Tin oxide,	5 ,,
Zirconia (or antimony oxide),	2 ,,
Magnesium oxide,	2 ozs.
Ammonium carbonate,	1 oz.

The melting of this enamel is very important, whereas in grey it is advisable to err on the side of over-melting, the frit for first coat should be withdrawn from the melting furnace at the first possible moment.

On grinding, a fairly high inclusion of clay is permissible, 7 to 8 per cent. being usual. Up to 40 per cent. of water is satisfactory, and the slop enamel should just pass a 50 or 60 sieve. If substitutes for tin oxide are to be used in the enamel, now is the time to employ them, and in general this stage is the enameller's playground where experiments are first tried. First-coat work is usually left in the hands of less experienced workers, and lower piece-work rates paid, providing a useful training ground for recruits. Its fusing department is often "nobody's baby," and is moved hither and thither to a ground-coat furnace which is dull, or a finish furnace which is too keen, or it may be used for completing odd loads, or alongside colour work. These are expedients which may be necessary in practice, however objectionable they may be in theory. Certainly the best result is obtained by having a complete organisation for each stage of the work.

Many faults begin to demonstrate themselves at this point, the majority belonging to the previous ground coat, or lack of cohesion between the two. Should the grey be too soft or underfired, blisters may now be expected, a somewhat similar result obtaining if the ware has been kept too long in the fused grey state. This applies particularly to enamels high in borax and other materials which absorb moisture from the air, this moisture being subsequently expelled in the form of steam on fusing the next coat, though most of it should be driven off during the drying process, if this is carried out thoroughly. Faults due to incomplete scaling and pickling often assert themselves now, for though they were naturally present at the ground coat stage, they may have been small enough to escape observation, whereas, now, appreciable areas show, and the article is fit only for the scrap heap.

Most of the strictures regarding drying, transporting, and fusing the ware, which were discussed in the previous chapter, apply equally or with more emphasis here. It is usually possible to set an article for drying and fusing in different manners, so as to minimise the effect of the inevitable spike marks.

Second Coat White.—The qualities generally looked for in the final white coat are whiteness and gloss. There should be a good white basis upon which to work, and all that is now necessary is the application of a glaze. Nothing elaborate in the way of raw materials is either necessary or advisable, it being falsely assumed frequently that the best enamels contain rare and complicated ingredients. The idea is entirely wrong, the best results being obtained from the simplest materials, success depending on their purity, and correct blending and manipulation. An excellent frit may be made from a mixture containing up to 35 per cent. borax, up to 40 per cent. felspar, moderate quantities of cryolite and fluorspar, quartz from nil up to 30 per cent. according to hardness desired, and the usual soda and nitrate. Such a recipe reads :—

Finish White.

Borax,	31·6	per cent.
Cryolite,	8·2	,,
Felspar,	37·2	,,
Potassium nitrate,	3·1	,,
Quartz,	13·7	,,
Soda,	6·2	,,
	100·0	,,

Mill additions to 100 lbs. Frit.

Clay,	6 lbs.
Tin oxide,	7 ,,
Magnesium oxide,	2 ozs.
Ammonium carbonate,	1 oz.

The frit should be thoroughly melted, leaving no risk of bubbling whilst being fused. Absolute cleanliness and attention to detail are essential to success. Grinding is continued until the wet enamel passes an 80 sieve, and all possibility of contamination is excluded. A thin application of enamel is essential, about 40 per cent. of water being employed. Many a good white is spoilt by tiny specks of dust and dirt accumulated during working, the fault being insufficiently grave to cause a reject, but the general standard of quality is appreciably lowered. Finished ware requires to be fused on its own by the highest quality labour available. In general practice the finished work gets more than its due share of attention, great efforts being made to cover faults belonging to an earlier operation, instead of devoting the attention to eliminating the cause. At the same time, praise is accorded to the enamels and workers employed at this stage for producing results which would have been impossible but for the excellent foundation. An important point at this stage is to have an enamel which forms a hard biscuit, as it usually has more handling for badging, branding, etc., than other work.

Spraying or Aerographing.—By spraying is meant the application of the enamel in a fine jet by means of compressed air. The process is simply one derivation of the system originally intended for paint, but now applied to many industries, including the spraying of molten metals such as aluminium on to a steel surface. For enamelling, the " pistol " is held in the hand of the operator, and is fed with the liquid enamel and the compressed air. Working in conjunction with the compressor is a fan to extract the enamel dust and mist from the atmosphere. Where a direct comparison is made between the costs of enamelling, in the case of an article which may be treated either by dipping or spraying, the latter averages 50 per cent. dearer for labour, and is more extravagant with enamel, but it has special application for work too heavy for dipping, for perforated articles, such as colanders and soap racks, which do not cover evenly on dipping, also where different thicknesses of enamel are required on a multiple blank, and it is indispensable for repair work. A finer ground enamel is necessary and less clay may be used, and with careful handling a first-class finish is obtained, superior to that with a dipped article. The process is more easily learnt than dipping, and is a useful adjunct where the apparatus can be fully employed and the extra expense justified. For flat work, such as hearth and sign plates, spraying has become indispensable, its specialised action enabling many colours to be applied without necessitating a separate fire for each.

One Coat Finish Ware.—The difficulties to be encountered on endeavouring to produce a finished article with one coat of white only over the ground coat, have been indicated at the head of this chapter, yet, on the other hand, since durability is achieved by the least possible quantity of enamel, this is in favour of the minimum number of coats. In practice, however, to produce the necessary covering power a thick coat of enamel is necessary, and the saving between this and two thin coats is not appreciable in this respect. Technically, the process is difficult in the extreme, yet remarkably creditable results are obtained, with the production of only a small percentage of second quality finish. What constitutes a reasonable percentage of "seconds" depends entirely upon the quality desired and the market aimed at, consequently no hard and fast figures may be stated, but where 3 to 5 per cent. are regarded as normal for two coat ware, 10 per cent. for one coat is not unreasonable where similar care is applied.

The only outstanding alteration in the composition of the enamel is the increased content of tin oxide necessary, which is expensive, and weakens the enamel, more particularly as a thick coat is necessary. The general practice is to keep the cryolite as high as possible —that is, in the neighbourhood of 15 per cent.—borax is maintained fairly high to produce the necessary gloss, whilst felspar and quartz will be manipulated to suit the temperature which the metal will withstand.

A useful one coat recipe reads :—

One Coat White.

Borax,	28·3	per cent.
Cryolite,	16·3	,,
Felspar,	34·0	,,
Potassium nitrate,	6·1	,,
Quartz,	15·3	,,
	100·0	,,

Mill additions to 100 lbs. Frit.

Clay,	6 lbs.
Tin oxide,	10-12 ,,
Magnesium oxide,	2 ozs.
Ammonium carbonate,	1 oz.

The batch is melted quickly and withdrawn at the earliest possible moment. Generally no addition such as cobalt oxide is necessary to neutralise the iron tint, as the blue-grey of the ground coat will do this. The wet enamel must not be ground so fine as ordinary finish enamel, but should just pass a 50-mesh sieve, 30 per cent. of water being used. Fusing is conducted in a sharp furnace.

One coat work requires an organisation of its own; it is useless to transfer dippers from two coat work and expect good results. Normally, the best workpeople will be required for this class of work, and once accustomed to it should not be moved. Where strict attention is paid to limiting the shape and size of articles to those of the simplest type, possessing no large areas of uninterrupted white, nor tortuous angles and seams, a quite respectable finish may be produced, suitable for export or ungraded home quality. That this is successfully accomplished is demonstrated by the increasing output of one coat ware.

The foregoing remarks have no reference to the lining of such articles as kettles with one coat of white enamel. Here the interior is so dark that a pure white would not show to advantage, and since durability is of paramount importance, one coat of enamel is both usual and preferable.

The finishing-off of white hollowware by edging the bead with coloured enamels, such as navy blue or black, or occasionally red, improves the appearance and renders the article less liable to chip. This is done whilst the white is in the biscuit state, and may be carried out either in first coat or second, whilst at least one prominent continental manufacturer tips directly on the iron, before the ground coat is fired. The advantages of early tipping are the elimination of water marks (the running of the coloured enamel into the white), and the prevention of firing in any white which may be accidentally left on the bead, and upon which the coloured tip will not take. The difficulty is to produce a blue enamel which will stand the two or more fires it will have to endure. Tipping enamels require to be rich in borax to produce the necessary gloss, and yet be sufficiently durable not to chip. The method of application varies with the article, it may be applied by hand, or the enamel squeegeed on to a glass plate, and the article rolled upon it. A good bold bead enhances the value of an article considerably, and false economy is frequently practised by using an anæmic-looking enamel for the purpose.

Before leaving the subject of white enamels, mention may be made of the effort to produce enamels containing no borax or boric acid. These borax-free enamels became almost a necessity in Central Europe during the war, when this material became scarce, and since borax is above the average of the ingredients in cost, the perpetration of so-called substitutes has continued. There is, however, no substitute for borax, its elimination meaning a recasting of the formula with a higher content of soda. All experience with borax-free whites leads to the conclusion that it is impossible to produce a highly lustrous enamel without its aid. Two typical recipes follow, and the results they give are characteristic of this type of enamel, indicating that an enamel made with no borax or an inadequate proportion may be recognised immediately by its dull finish.

Borax-Free Whites.

(1)			(2)		
Cryolite,	11·5	per cent.	Calcium carbonate,	3	per cent.
Felspar,	34·6	„	Cryolite,	13	„
Quartz,	34·6	„	Felspar,	30	„
Soda,	19·0	„	Fluorspar,	9	„
Sodium nitrate,	0·3	„	Quartz,	22	„
			Soda,	20	„
	100·0	„	Sodium nitrate,	3	„
				100	„

Coloured Enamels.—Attention was drawn in an earlier chapter to the limited range of coloured materials available for enamelling, since all vegetable and coal-tar dyes, and most other colouring matters, are either destroyed or decomposed at enamelling temperatures. Nevertheless, within these narrow bounds, it is possible to produce a complete range of tints. Some few colours present difficulties, a true emerald green being expensive, and pink, both expensive and not a very rich tint. With these minor exceptions, all colours of the rainbow are available.

The colour is produced in either of two ways ; it is fritted with the enamel, or added as a mill addition. The principal colouring matters employed are cobalt oxide for blues, chromium oxide for greens, iron oxide for browns, manganese, cobalt, nickel, iron, and chromium oxides for black, cadmium sulphide for yellows, and this with selenium for red.

Frits for Colours.—These are of two types, one a transparent, colourless frit for use with the lighter colours, the other a self-colour frit, or one tinted to assist the production of the final colour. The delicate colours almost invariably require two coats of enamel, and here the choice of two alternatives is offered, an enamel rich in colour may be applied over one coat of white, or both coats may be tinted to a lesser degree. The former provides more delicate shades and offers a slight advantage in costs where an article is to be coloured outside and white in, since it may be enamelled all over first time, with a consequent saving of an operation. The disadvantage is any flaw in the final coat shows the white through, and is in consequence aggravated, whereas if two similar coats of colour are employed minor faults are hidden. Where a first coat of white is applied, the normal first coat white enamel fills the role satisfactorily, and is frequently used in conjunction with a pigment where two coats of colour are applied. There are, however, many advantages to be gained from the use of a separate frit. The primary function of a first coat white is opacity; this is of little use in colour production, as here transparency and gloss are the chief requirements, and judged by the normal standard the frits require to be deliberately over-melted, an expensive process which is sometimes resorted to being to return the frit to the furnace and remelt it. The influence certain frit ingredients have on colour production has been previously indicated in Chapters III. and IV., and particularly boric acid, the fluorides, and zinc oxide. A simple mixture for a frit for light colours reads :—

Base for Light Colours.

Borax,	27	per cent.
Felspar,	30	,,
Quartz,	12	,,
Soda,	2	,,
Sodium nitrate,	3	,,
Clean white waste,	26	,,
	100	,,

The darker colours are usually produced from a coloured frit, and in the case of blue and sometimes green and black enamels, no other addition of colour is made. Generally the use of a prepared colour at the mill is advisable, and often essential, as fritting would spoil the colour. Should a white frit be used for preparing a dark colour, a speckled appearance may result, which, if not visible to the naked eye, may be seen under a magnifying glass. These frits present a good opportunity of using up odd enamel and dried waste.

The prepared colours which are available for addition to the mill are generally described as "colour oxides," this description being chemically true. These were formerly obtained largely from continental sources, but the whole range is now made in English works which export appreciable quantities to the continent. These colours can be made in the enamelling works, but it is not a policy which can be recommended. Where an appreciable number of colours is required, a corresponding number of grinding mills is necessary, and the manufacture requires close attention, scrupulous cleanliness, and a high degree of purity of ingredients. Further, the colours require to be made in fair quantities to ensure continuity of colour, and this involves appreciable capital. When all these requirements are met to perfection the result compares unfavourably with that produced by the skill and experience of the specialised manufacturer. The percentage of these colour oxides employed depends entirely upon their strength, and the colour desired. Frequently the lighter colours are used in conjunction with tin oxide. Where the latter is replaced by a substitute, it must be borne in mind that if this latter has acidic or alkaline properties it may affect the colour. Exact continuity of colour throughout a number of months is extremely difficult with the delicate colours, consequently it is bad policy to do bulk quantities of such articles as tea pots at one time, and the lids at some later date. Most of the colour oxides are employed on hearth plates and sign plates, and here it is generally immaterial if slight variations in tint occur from one batch to another. Colour oxides should be supplied in a very fine state of division, and should be ground with the frit until it passes an 80 mesh. The maximum colour effect is produced by a preliminary grinding of the oxide wet with the clay and part of the frit. The exact shade of colour is affected materially in the fusing, consequently standardised furnace conditions must be maintained, and, as far as possible, only one colour allowed to be in the furnace at the one time.

The best practical test for colours employed in sign-making is the exposure of a sample plate to the atmosphere. One such plate exposed on a factory roof for two years to sun, rain, wind, snow, soot, and fumes was none the worse for its experience.

The various coloured enamels will now be considered in alphabetical order :—

Black.—A popular colour, particularly for the outsides of domestic ware, and to the sign-plate makers for contrasts and shadows. A black enamel may be made by fritting a batch containing the coloured material without the addition at the mill of a prepared body, but a dead black is seldom prepared this way, and a colour oxide is necessary for correction. On the other hand, one sees brilliant blacks made from a transparent frit with a higher percentage of colour oxide. A good black is the most difficult colour to produce ; many samples look good until placed alongside jet black, when they are all either blue-blacks or brown-blacks. The prepared colours vary in price and quality enormously, and the best result is obtainable by using a coloured frit which is likely to be on the blue side, and adding a small proportion of a good prepared colour to compensate. The ingredients mentioned for making black enamels are all fairly refractory, consequently the best results are obtained by fusing in a good sharp furnace. The necessary result should be obtainable with one coat ; in fact, for domestic ware, it is usual to economise by dipping the inside with the lighter colour first, then drying and dipping the outside, the whole being completed with one firing after the ground coat. No further additions to the frit except clay, the colour, and probably a little magnesia are necessary.

Blue.—Blue enamels are of two classes, those produced by adding cobalt to the frit, and those produced from mill additions of prepared colours. The former generally constitute the dark blues, and the latter the light blues, though cobalt may be fritted to produce any intensity of colour. In addition to flat work, dark blue finds employment like black for cooking utensils, backs of dinner plates, water bottles, and army requirements generally. Where a dark blue is used in conjunction with a white enamel the same recipe may be retained, and a suitable addition of cobalt made. In this case boric acid should be present, and the affect of fluorine may influence the blue. The most intense blue should be obtainable with 2 per cent. of cobalt oxide, and this used in one coat. If more than this quantity is necessary, the colouring power is not being fully developed, and changes in the frit are necessary. The grey, prepared cobalt oxide is recommended for colour making, producing purer blues than the ordinary black oxide.

Light blues are generally made from a colourless frit, and the cobalt blue obtained from a prepared colour containing the cobalt suitably fritted. Cobalt gives such an intense colour that ½ per cent. of these bodies is usually ample. For light blues, tin oxide is generally a constituent, and for high quality work two coats are necessary. A reasonably dark blue can be obtained by this method, an acceptable royal blue being capable of preparation, but for a deep rich blue such as that required for tipping, fritting is necessary. In addition to cobalt, chromium oxide is sometimes employed to produce the blue-green series. Blue is the most consistent colour in the furnace, and exact shades are easily reproduced.

Brown.—This is another favourite colour for the outside of cooking utensils, all shades from a red to a grey being available. Most brown enamel is obtained from a coloured frit, though light browns may be made from white, both being used in conjunction with a prepared colour largely composed of iron oxide. Iron oxide may be obtained in many shades according to the heat treatment (that is, temperature duration and atmosphere) to which it has been subjected. For the purposes of a pigment it is required to be in the highest possible state of purity, and is usually obtained by igniting a pure iron salt. The likely impurities have been discussed on p. 50. For the darker shades it may be associated with manganese or chromium oxides.

Cream.—*See* Ivory.

Green.—Here again a wide variety of shades is available, the dark greens being made from a special frit, occasionally the ground-coat grey being employed. All the best greens have their basis in chromium oxide, and this may or may not be fritted. The advantage of the former method is that the oxide loses none of its colouring power, and is completely incorporated in the enamel, if thoroughly fritted. If used as a mill addition, its high melting point is liable to act against the production of glossy enamels. In the extraction of chromium oxide from chrome iron ore, the sodium chromate is deliquescent, and consequently this is usually converted to potassium chromate by treatment with potassium chloride, and this potassium chromate completely ignited with sulphur. Unless this is done thoroughly the original salt remains and causes a dull finish, and the presence of this impurity may be detected by shaking with water and allowing to stand ; the upper liquid layer should remain colourless, a yellow colour indicating undecomposed salt. Chromium oxide should also be tested for the presence of sulphate.

Lighter shades are obtainable by mixing with tin oxide, antimony oxide, or cadmium sulphide, and other varieties are obtained by the use of blue and black oxides. Another green pigment is *Rinmann's green,* made by igniting zinc oxide and cobalt oxide. One coat of a dark green is usually sufficient for all practical purposes, and this coloured enamel is usually easy to work.

Grey, Pearl, etc.—These colours are made from the same materials as black, used as a mill addition at considerable dilution with a colourless frit.

Ivory, Cream, etc.—Apart from flat work, these light tints find favour for the lining of culinary ware. They are more serviceable than white in the same way as tinted wall papers are more durable than a pure white ; they do not show the stains so readily. The pigment is made from the brown or yellow at considerable dilution, and generally in conjunction with tin oxide.

Orange.—This is another of the decorative tints, and is not a basic colour, being made by the addition of red to yellow, a process which may be accomplished at the works, and all shades between these extremes are obtainable by simply altering the proportions. Consequently the remarks applying to red and yellow apply also to orange enamels.

Pink.—This is the least satisfactory colour from the enameller's point of view, and is consequently the colour most seldom seen. There are two types of pigment, the tin-chrome and tin-gold, though it is well known that genuine purple and pink shades can only be obtained by the use of gold. Tin-chrome is infinitely cheaper, but does not produce a colour of sufficient intensity. It finds a limited employment for the elaborate decoration of articles for the Far East. The tin-gold pigment is the long known Purple of Cassius, and is naturally an expensive substance, costing £2 to £3 a lb. It is, as explained in Chapter IV., the colloidal gold on tin oxide obtained by precipitating stannous and stannic chloride with gold chloride. Different shades are obtained by using magnesium, aluminium, etc., compounds in place of the tin oxide. It produces lovely shades when used up to 5 per cent. with a transparent frit.

In a somewhat similar category fall the lustre colours which are so popular in pottery to-day, but have yet to be developed for enamelling. These depend on gold or silver salts together with a bismuth basis, and are thus expensive. They require firing at 600° C. in a reducing atmosphere.

Red.—This is the most interesting of the colours. At the present time a pigment made by heating cadmium sulphide with selenium is universally adopted, and can be obtained in all shades from bright vermilion to deepest crimson, the larger the percentage of cadmium the brighter the red. Cadmium sulphide is not a substance particularly resistant to heat, and selenium is a black non-metallic element resembling sulphur in many respects, which melts at 217° C., and costs about 15s. a lb., yet these two substances when heated together produce a beautiful and permanent red. The colour is difficult to prepare, and requires absolutely standard furnace conditions. It is always added as a mill addition, and a special frit must be made to suit it. Potassium and sodium nitrates should be minimised, since they discolour the red, and as an iron-tinted frit is no objection in the present instance, their presence is not required. With the exception of pink, red is the most expensive colour to produce, and is the most sensitive. Acid fumes affect it, and even a rusty piece of iron such as a spike coming in contact with the enamel will discolour it. Similarly, perspiration from a workman's hands will leave a mark. Furnace conditions require to be absolutely standard, and as low a temperature as possible should be used for fusing.

Yellow is made almost exclusively from cadmium sulphide, though molybdenum and uranium compounds may be employed, and lead antimonate (*Naples Yellow*), also where a poisonous enamel is no objection. Cadmium sulphide, CdS (M.W. = 144), occurs naturally as the mineral *greenockite*, but for enamel purposes requires strict purification, and is, therefore, always obtained finally by precipitation from a solution containing a cadmium salt. According to these conditions of precipitation the colour may vary from lemon to orange, and for colour-making a cadmium-carbonate sulphide is preferred by many, this being obtained by precipitating the carbonate and sulphide simultaneously from the same solution. The chief consideration, where using cadmium sulphide, is to ensure that all excess sulphur is removed. Cadmium sulphide is used as a mill addition, and is a very strong pigment, 1 per cent. producing an intense colour. It may be used in conjunction with an ordinary white frit, or a special transparent one, tin oxide being added frequently to produce a softer shade and greater brilliance. Low temperatures for fusing are essential, as a slight elevation in temperature produces a porous effect resembling, and known as, "orange peel."

Gain in Weight on Enamelling.—Reliable statistics on this topic are difficult to produce, since they depend on the gauge, size, shape, and weight of the article concerned, and also the method of applying the enamel. The figures which follow apply to flat sheets of about 1 square foot in area, any increase in size showing an increase in the percentage of enamel, the extra weight acting against energetic dipping with consequent thicker coats. For the same reason heavier gauge material has more enamel on it, yet, against this, the same thickness of enamel, on a heavy gauge sheet naturally appears as a lower percentage in a weight basis, as the weight of steel is so much greater.

TABLE XIV.—VARIATIONS IN WEIGHT DURING ENAMELLING.

	Percentage on Weight of Iron.		Percentage on Finished Weight.	
	18 Gauge.	28 Gauge.	18 Gauge.	28 Gauge.
Loss in Weight on Pickling,	1·3	2·9	...	...
Gain in Weight, Ground Coat,	2·4	14·0	2·2	9·0
Total Gain in Weight, One Coat Finish,	...	56·0	...	36·0
Total Gain in Weight, Two Coat Finish,	9·1	65·5	8·3	39·8

Branding and Badging.—In addition to customers frequently requiring a trade mark imprinted, manufacturers are branding their ware in increasing numbers. If the design is at all intricate, a transfer is necessary, and is applied to the glaze, requiring another fire; similarly, if very bold letters are required, an extra fire is necessary, the application in this case being made by oil first, and the printing powder dusted on. For simple work, blues and sometimes blacks and reds may be applied to the biscuit by means of a rubber stamp and pad soaked with a water solution of the appropriate substance. Cobalt and nickel salts are suitable for this purpose, the advantage of water as a medium over oil being the absence of blistering occasioned by the latter.

In a works dealing with numerous white enamels of different qualities for different purposes, these may be readily distinguished by adding minute quantities of different colouring matters to them. Colours are selected, of course, which burn off and leave a dead white on fusing, and insufficient is used either to affect the enamel or the workers' hands. In the selection of colour, it must be borne in mind that the alkali of the enamel will destroy certain dyes, and also that clays have the ability to absorb them, and consequently the first addition may not be visible. This absorption of dyes by clay is, in fact, one of the methods of measuring its physical properties, Dyes of the type of malachite green are satisfactory for staining enamels.

Faults and their Remedies.—The old dictum that 'advice is cheap' applies with much force to enamelling, and when an enameller acts upon some of it which is forced upon him *gratis*, he usually lives to learn that it has changed hands for more than its market value.

Defects in enamelled ware are frequently difficult to explain in a few words, and are often not due to the first cause hurriedly assigned to them. They may be divided into two classes; routine defects, generally of a minor character and which appear and disappear periodically, and new and unprecedented ones due to some specific and unidentified cause. The vast majority of faults are due to wrong manipulation, those being due to errors of technique being few in number and generally easily remedied. This is not to be interpreted as meaning that it is an elementary matter to convert a defective enamel into a perfect one, as in most cases much knowledge and experience has been necessary to produce those of the standard we accept as satisfactory to-day. When faults due to manipulation do occur, it is generally useful to think twice before (or after) blaming the worker concerned. Under the systems and facilities often provided accidents can only be avoided by a fuser proving himself to be an apt disciple of Maskelyne or Cinquevalli.

Another may be blamed for smudging work, when the biscuit ware is so soft that it is almost incapable of movement without disastrous results. Certainly a very high standard of care and attention to detail is essential in all enamel works, but the limits of human capacity should not be forgotten.

Where a new and peculiar fault arises, prompt action is essential where routine work is in progress, or thousands of pieces may be spoilt. The quickest solution is generally obtained by a thorough investigation of all stages of manufacture concerned, and not by haphazard shots at possible causes. By thorough investigation is meant the responsible person going into root causes himself and trusting nobody else to help even with the donkey work. The silliest mistakes may be made and repeated unconsciously until discovered by another investigator.

An example of one type of defect was a persistent blistering which could not be traced until it was discovered that clay and sodium nitrate were being kept in adjacent bags, the latter taking up moisture from the air, and the liquid soaking through and mixing with the clay.

Many possible faults and their remedies have been mentioned in the course of this work, such as the pits in the ground coat due to excessive or undissolved borax, black spots in white enamel due to reduction of the tin or antimony oxides, the orange-peel effect of over-firing cadmium sulphide ; and blistering due to applying a harder enamel over a soft one. Faults due to steel have been mentioned in Chapter I., and are generally obvious. Incomplete cleaning leads to bare patches of appreciable size and necessitates the ware being de-enamelled or scrapped. Undermelted enamels give a dull, lustreless finish, and may blister. Overmelted are generally dirty and lack body, the result being like glass. Under-fired enamels in grey remain blue, and are lustreless, rough to the touch, soft, readily detached, and bubble up when another coat is given. Over-fired ground coats are porous, or, in extreme cases, bubble and skin at the edges.

The specific troubles commonly found in grey enamels due to faulty composition include failure to hold on to the beads of articles, with resultant flying off when another coat is applied. This is generally caused by scamping cobalt oxide. Fish-scaling, the name given to the flying off of small pieces of ground coat, frequently after a lapse of hours or days after fusing, is fortunately rare in this country, though it appears to be the bugbear of American enamelling. The name is taken from the appearance of the pieces which come away, and is presumably due to the different composition of enamels favoured by Americans, the chief distinction being their high lime and fluorine contents. In the course of an investigation on some fish-scales deliberately produced, it was found that the fault was remedied by increasing cobalt oxide, and also quartz at the mill. This is not claimed as a specific cure for all fish-scaling, as the necessity for meeting this trouble has so seldom arisen.

Finished enamels bearing patches and no lustre, point to a leaky muffle, excessive salts, or the introduction of some impurity, and enamels which lose their gloss after wetting or on standing some time also indicate excessive salts, excess soda, or incomplete melting, and may be remedied by remelting the frit.

A vein-like formation, apparently below the surface, sometimes referred to as trees is the result of applying enamels too thickly, whilst deeper lines or cracks indicate too hard an enamel. Crazing, the appearance of hair-like cracks, is due to an enamel having too great an expansion, and may be cured by reducing cryolite and increasing borax.

Where hollowware is packed too closely, and in heavy stacks, the pressure may cause fine, almost invisible cracks in the enamelled surface. If this is enamelled further or subjected to rough handling, whole areas of enamel may peel off.

De-Enamelling.—De-enamelling is the removal of the enamel from the finished article, leaving the steel blank uncovered, and ready for enamelling again. The process is useful where a mistake has been made with a special article, and generally where the more expensive articles have been spoilt and are wasters. It cannot be recommended for the ordinary range of domestic hollowware, which has perhaps not come quite up to expectation. The process is also useless for deciding on a point of fact whether a fault has been due to bad iron or bad enamelling, because defective iron after the drastic process of de-enamelling will usually cover perfectly at the second attempt.

The process is essentially a chemical one, and since the prime object of enamelling is to produce a resistant coating, the complete removal of the enamel is not a simple matter, but involves the use of highly corrosive agents such as strong acids or alkalies. Hydrofluoric acid will readily decompose any vitreous enamel, and other strong acids more slowly, but the disadvantage of these is that they also attack the iron, hence unless the enamelled surface is absolutely uniform in thickness throughout and contains no flaws, uneven action will result, with consequent destruction of the iron. Further, should the enamelling be absolutely uniform, the article must be withdrawn at the time that all the enamel has been destroyed, and before the iron is attacked. Because of these practical difficulties, acids must be ruled out.

Alkalies have the advantage of having no chemical action on the iron, and enamel may be removed by boiling the article in a saturated solution of caustic soda. The process is a very slow one, twenty-four hours continuous boiling being a minimum, and a more practical method is to employ the undiluted caustic in the molten state. Caustic potash, though slightly dearer than the corresponding soda compound, is preferable ; it melts easily below red heat to a thin liquid, and articles immersed in it are de-enamelled almost instantaneously. A cast iron bath over a coal fire is all that is necessary, though it should be kept indoors and absolutely dry, as the presence of water renders an already unpleasant operation decidedly dangerous, owing to spurting of the material on warming.

CHAPTER X.

FURNACES AND FUSING EQUIPMENT.

Mention has been made in previous chapters of the two types of furnace necessary, the one for melting enamel and the other for fusing the coat of enamel on to the metallic surface. The two conform to the general requirements of industrial furnaces and consequently have received more attention, and more progress has been recorded than in any other branches of the industry. The melting furnace is a simple reverberatory furnace, the batch being held in a box-shaped hollow, heated (except in the case of electricity) by the flame direct, and is similar in most respects to the furnaces used for melting metals. The fusing furnace is of muffle type and this again conforms to usual practice, an absolutely gas-tight muffle being essential. The usual fuels, coal, oil, gas, and electricity are available, coal being the most popular in this country. In keeping with the Americanisation of the enamelling industry, oil is finding an increased use, though it is unable to compete with coal on a cost basis, a rough estimate being that oil costs twice as much and goes once and a third as far, showing a net increase in fuel cost of 50 per cent. Its many advantages over coal are apparent, including ease of transport, adaptability and cleanliness, and it is naturally popular in America where oil is so much cheaper. Where this fuel is employed, fusing furnaces have been designed without muffles, thus saving fuel, but the presence of sulphur in the fumes has to be contended with, and muffles are still general practice.

Town gas supply is unquestionably too expensive for heating anything but the smallest furnaces, but producer gases, which are a commercial proposition, are available in some districts. Producer gas is obtained essentially by heating coke in an insufficient supply of air for complete combustion, and a similar fuel, water-gas, is obtained by using incandescent coke again, but steam being substituted for air. The former is mainly carbon monoxide, the second a mixture of carbon monoxide and hydrogen. The more usual practice is to produce the gas from coal in the works itself and to burn it in the furnaces. Two systems for doing this are available, one central producer for the whole works with mains laid to the desired points, or a producer in each furnace. Though the former is possibly more economical of coal and labour, the latter has the advantage of not requiring a pipe system, and full advantage is taken of the heat, there being no heat lost during transport of the gas. Further, in the event of a breakdown in the case of a central producer, the whole works is stranded. Electric furnaces represent the ideal, but so far are only at the stage of being a hope for the future. They are economical of space, require no dirty fuels, and are capable of absolute control of temperature and may be placed at any convenient point in the works independent of a suitable dumping ground for fuel. Electric furnaces are usually of the resistance type, *i.e.*, wound round the top, bottom, and sides with wire coils through which the current passes. Their advocates claim that the power consumed is no more expensive than other fuel, though this is not in accordance with the general opinion. The fuel cost is more easily determined when using electricity, though maintenance charges must include the possibility of the wiring fusing and requiring replacement.

Where coal is selected it is necessary to dispose the furnaces where it can be conveniently tipped, and the ashes readily removed. Labour charges for handling coal will materially affect the economic position, and as flue construction is an expensive procedure, skilful planning initially is advisable. The only chemical requirement regarding coal is that it shall be low in sulphur, that is, in the neighbourhood of ½ per cent. The type of coal most suitable is long flame, non-caking, and possessing a calorific value of 7,500 (equivalent to 13,500) B.Th.U. This is readily obtainable from the Warwickshire, South Staffs, and other mines. It is the type of coal required for blast furnaces, or the gas coal used largely in reverberatory furnaces, and is better quality than ordinary furnace or household coal.

Too large stocks of coal are not advisable owing to ‘slacking’ which results in the simultaneous loss of some of the combustible gas. The direct firing of furnaces by coal has been largely superseded by more economic methods of fuel consumption, these including the more complete combustion of the fuel, and the use of the waste flue gases. These objects are generally achieved by regenerative or recuperative methods. Regenerators are chambers—two are required, one on either side of the furnace, fitted with chequered brickwork. The hot flue gases from the furnace are first passed through one of these on the way to the stack, and when the bricks are thoroughly heated the direction is changed, and the exit made through the other regenerator, air being drawn through the heated one and used for the combustion. The direction is changed periodically, usually at about hour intervals, and so the heat exchange is obtained. Recuperative methods depend on passing the waste gases through fireclay tubes round which the necessary air for combustion is drawn, and this method consequently has the advantage of not bringing the air into contact with the waste gases and is therefore cleaner. The heat exchange in either case cannot be carried to the logical limit of extracting all heat from the flue gases, since a minimum temperature of 300° C. is necessary at the foot of the stack to enable this to draw, unless a forced draught is employed.

Recuperative furnaces are usually associated with a gas producer, wherein the coal is distilled rather than burned, and this volatile matter meeting the hot air burns with a hotter flame. Not only does this more efficient combustion ensure economy of fuel, but it is far more healthy in materially reducing the smoke produced from the chimney stack. Black smoke, which merely represents unburnt carbon is harmful, and a mark of inefficiency. A thin smoke is not to be objected to since it ensures that a reducing atmosphere exists in the furnace. Machines known as carbon dioxide recorders are available for insertion in the stacks and flues for indicating whether the furnace is working economically or otherwise. Temporary lapses during and following coaling and stoking naturally have to be allowed for.

A successful furnace built on the gas producer and recuperative principle is illustrated in Fig. 17. It is due to A. Hermansen and has achieved international success in enamelling and other industries. The various features of the furnace are :—

A. The ash pit.
C. The combustion chamber.
F. The flame flue.
L. The flue leading to the recuperator.
P. The water-cooled stepped grate producer.
R. The recuperator for heating the air for combustion.

By the application of these methods the coal consumption on muffle furnaces may be reduced by 30 per cent., and as these furnaces are usually constructed on better heat-conserving principles, the saving may amount to 50 per cent.

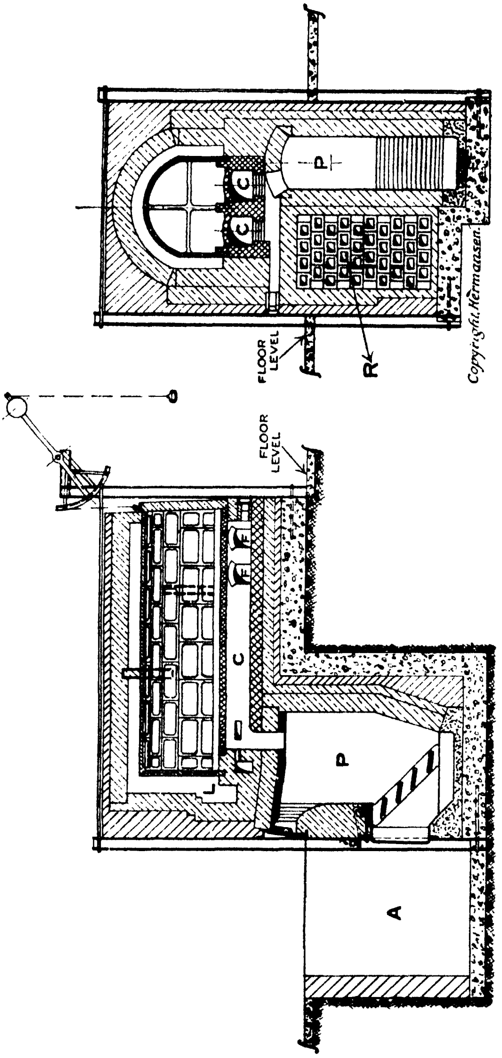

Fig. 17.—Recuperative Furnace (*Hermansen*).

Direct firing on melting furnaces is grossly inefficient, the fire box gaining most heat and the melting bath being dependent on the obstruction offered to the passage of the flame through it. Obviously a short flame will not heat the batch uniformly, whereas a long flame gives part of its heat to the flues. The coal consumption on a direct-fired melter may well exceed 30 cwts. per ton of frit obtained, whereas the figure for a recuperative melter should not exceed one third of this figure. A better conservation of heat is obtained by the use of the many insulating materials available for inclusion in the walls of furnaces. These generally have a basis of magnesia or silica or both, and are light and porous. America possesses mines of these materials in a high state of purity.

With the majority of recuperative furnaces, the draught may be accurately regulated, and consequently the heating is under better control, with more uniform temperatures. Stoking requires intelligence, and the ‘little and often law’ must be obeyed. Most of the furnaces are designed to burn a proportion of slack or poorer fuel if desired.

The size of the melting furnace has been considered in Chapter VII. The dimensions of the muffle will depend entirely on the class of work to be handled, and it is easy to fall into the false economy of having furnaces too large. The usual width for a furnace dealing with holloware or flat work is 4–5 feet for the inner muffle, whilst 15 feet is an outside limit for length, 10–12 feet being more usual. The height requires to be 3 feet to the crown for holloware, but lower furnaces suffice for flat work. For factories persistently on small work such as tablets or stove parts, much smaller muffles are economical, whilst at the other extreme household baths, or large chemical pots require appropriate sized muffles. Furnaces having the dimensions given above will generally keep two men fully occupied.

The method of loading a furnace by the usual type of fork is open to the criticism that the furnace stands idle whilst this is unloaded and recharged, and for many years systems of obviating this loss have been tried, though it was not so important in the old days, since the earlier furnaces did not produce enough heat to withstand continuous fusing. This has now been overcome and the simplest method of accelerated fusing is by means of a double set of fire bars ; the fork on being withdrawn from the furnace is turned on one side to deposit a load, after which another is picked up from the other side where it has been previously prepared. This has proved fairly satisfactory wherever the work is of a simple nature and can be handled quickly. For the average run of hollowware it must be written down a failure, since success in this class of work depends entirely on being able to return a load to the furnace whilst the fire bars are still hot, and this is usually impossible with the double load, despite the improved methods of mechanical operation which have been introduced. In the same direction criticism must be made of the elaborate fire bars devised for accommodating larger loads. They are generally difficult to charge, leading to delay in loading, and more damaged ware, and though they carry more ware, the fusing time is longer owing to the excessive amounts of iron to be heated. Double decking of the load had to be abandoned long ago here for anything but flat work, owing to the scale dropping on to the lower row of articles. The newer American methods render this possible by using far softer enamels, and consequently lower fusing temperatures. The fire bars are sprayed with molten aluminium, which prevents rust formation and consequent scaling. This process is no use for the typical steel enamels used in this country since at these temperatures the aluminium melts and fails to serve the desired purpose. A recent attempt to speed up the fusing process which is more applicable to electric furnaces is the idea of having a door to the muffle, either end with two forks and two sets of men working the furnace alternately. Attempts have been made to speed up production by the use of continuous melting and fusing furnaces. The idea of continuous melting is not new, but the production of a uniform frit by this means has yet to be realised, any system which permits the melted borax to run out of the furnace without the opportunity of dissolving the refractory material is bound to lead to mixed frits of all degrees of hardness. The continuous fusing furnace has made headway in America, working on the principle of the endless belt. The difficulties include the discovery of a material for the belt which will withstand constant heating and cooling whilst exposed to the air, and also a mechanism sufficiently delicate and smooth in motion not to damage the ware on fusing. Electric power is the most suitable method of heating, by means of which a regular gradation up and down may be obtained. Slow cooling has the advantage of preventing crack formation in the enamelled surface, and should produce more opaque enamels, though devitrification has to be guarded against. The type of furnace just mentioned is fundamentally a tunnel furnace, and is of course ideal for annealing.

The manipulation of the furnace door is a matter for serious consideration. Since this is either cast iron or a combination of cast iron and fire brick, often 8 inches thick, it possesses a substantial weight, and must be capable of easy movement. The usual method of opening is lifting vertically by means of levers and counter-balanced weights, though the objection to this is the risk of dirt falling on the ware. The disadvantage of dropping downward is that the load cannot be conveniently inspected. Opening outwards is generally impracticable and causes unwelcome draughts. The most modern doors are made to slide sideways and are operated by simply switching on the necessary electric power.

Furnace Linings.—The actual materials selected for furnace linings are fairly numerous, though chemically they are composed of a very limited number of substances. Their function is to withstand the destructive action of high and varying temperatures, oxidising and reducing atmospheres, abrasion, and in the case of melting furnaces the chemical action of the frit, which is by far the most active cause of destruction. The materials available include silica, alumina, bauxite, fireclay, and such combinations of them as *mullite* and *sillimanite,* together with *carborundum, chrome, magnesia,* and *dolomite.* When reading of the qualities of these materials one feels inclined to stop after having read about the first, feeling that the ideal has been attained, and that it is useless to enquire further ; the second material, however, is claimed to possess many more virtues, whilst the third finds employment where the second is unsuitable ; and so on ; the truth being that all have qualities and drawbacks peculiarly their own. Silica is well capable of withstanding the temperatures encountered, but suffers from the disadvantage of expanding appreciably on heating. For this reason great care has to be taken on getting a furnace up from cold, a gradual heating being spread over some days. P. B. Robinson * says that the thermal expansion of silica bricks is due to the properties of the three constituents, *quartz, crystobalite,* and *tridymite* present, and that serious expansion is met with only in under-burnt bricks, or in well-burnt bricks under 300° C. He recommends slow heating up to 600° C. The thermal

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* "*Chemistry and Industry,*" 4-xii.-25, p. 1181.

conductivity of silica is much higher than that of fireclay.

Fireclay is a fairly indefinite term including the combinations of alumina and silica capable of withstanding a temperature of 1,650° C., and varies considerably from the formula for clay Al_2O_3, $2SiO_2$ (all water being driven off below 500° C.). It is generally found near coal fields, as for example, at Stourbridge, Worcestershire, and is the most common of refractory materials. The higher the alumina content of the clay, the less trouble there will be with expansion, hence the more suitable for furnace construction, particularly recuperators and regenerators which are subject to sudden temperature change.

Pure alumina is very highly refractory, its melting point being 1,880° C., compared with about 1,600° C. for silica (this melting point is not very well defined), but it is an expensive material. Bauxite is a mineral consisting of impure alumina combined with water. A brick made from bauxite material found in Ayrshire and containing 45 per cent. alumina and 47 per cent. silica, was the only one to approach the Grade I. standard of the refractory research committee of the Society of Glass Technologists.

Sillimanite is a definite compound of alumina and silica in the proportion of SiO_2, Al_2O_3, that is, a higher content of alumina than in ordinary fireclay, and has a melting point of 1,815° C. Since various combinations of alumina and silica occur as minerals, sillimanite is made artificially from them, and bricks made from this artificial material are capable of withstanding 1,750° C., for prolonged periods and are being prescribed in increasing quantities for furnace lining, though they are comparatively expensive. A somewhat similar material is *mullite*, the formula of which is $2SiO_2$, $3Al_2O_3$, that is, higher still in alumina. This is an exceptionally inert and heat resisting product. It is made from raw material containing a high percentage of *grog*, and when a suitable mixture of alumina and fireclay is heated to at least 1,300° C.; mullite possesses great density and hardness. Sillimanite and mullite may be identified in fireclay in the portion insoluble in cold dilute hydrofluoric acid, mullite being easily recognised under the microscope by the lath-shaped crystals.

Carborundum is silicon carbide, SiC, and is produced when a mixture of coke, sand and salt is fused in an electric furnace at about 3,500° C. The manufacture is dependent on cheap power, and is consequently carried out at the Niagara Falls. It is one of the hardest substances known, and is consequently used for cutting and polishing. When made into bricks it finds employment in the construction of muffle furnaces owing to its high conductivity and resistance to high temperatures. Its advantages may be enumerated as given by C. G. Armstrong to the Chicago section of the American Ceramic Society:—

1. Its light weight and high conductivity enables a furnace to attain working temperature in 7 hours, instead of 3 days.
2. It facilitates definite temperature control.
3. There is much less loss of heat through the brick work, consequently flue temperatures are lower with corresponding longer life.
4. The lower flue temperatures permit a less bulky construction.
5. Greater fuel economy.
6. More uniform temperature is obtainable.
7. Over-heating is not injurious.

To which may be added that it is not attacked by any acid, sulphur fumes, saltpetre, nor oxygen at 1,000° C. It cannot be used for melting furnaces owing to the attack of molten alkalies. Its great difficulty, however, is expansion. The material in use becomes oxidised largely through flakes of iron oxide scale falling into the muffle, and this causes the carborundum to expand, and for this reason it is unsuitable for grease burning and scaling furnaces. Two cases have come to hand of carborundum failing for fusing furnaces ; the first muffle was constructed entirely of carborundum and the expansion was so great that the furnace eventually buckled completely, and required stripping, whilst more recently a muffle having a fireclay top and sides and carborundum bottom required rebuilding within six months owing to the bottom continually swelling until the flames broke through at many points.

The type of brick selected for use in muffles is always a box brick owing to its far greater surface, and consequent greater radiating area.

The chief requirement of the melter lining is the ability to withstand corrosive action at 1,200° C., at which temperature the alkalies and fluorides attack the silica and alumina of a fireclay lining. The enamel being alkaline, an acidic brick such as silica is out of the question, though it is excellent for use in the melter above the surface of the bath. A neutral brick is available in chromite, and is fairly resistant, though in the presence of silica the alkalies dissolve it, and consequently the batch is discoloured, though it may prove satisfactory for melting coloured enamels. A basic brick made from magnesia has an excellent life, is white, and of course very light. It is extremely expensive, and tests are now proceeding to see whether the increased life warrants the increased expense. The usual lining for melters is fire brick, and all other things being equal a high alumina content is distinctly advantageous. The origin of attack is the joints between bricks, particularly at the surface of the enamel batch, consequently the fewer the joints the better, hence the largest possible blocks are preferable to the ordinary sized bricks.

Immediately a joint becomes destroyed, two new surfaces of the brick become exposed to the attack, consequently tight joints are necessary. These require bricks of perfect shape, hammered together so that the thickness of the joint does not exceed $\frac{1}{16}$ inch. Materials of the same composition as the bricks are generally supplied as mortars.

The conditions and composition of enamel vary so enormously that it is impossible to state a hard and fast output of enamel a furnace should produce without relining; for example, a white enamel is generally more potent in attack than a grey owing to the higher fluorine content, but one hundred tons should be regarded as an absolute minimum. The enamel can only be heated from the top and sides since no material is available which is thick enough to support the weight of the batch, and yet thin enough to allow the heat to pass through.

A novel type of melting furnace well worthy of mention is the rotating melter, which again is of American origin, though reports have appeared of another from a German source. The American furnace has oil as fuel, though it should be equally suitable for electricity or even coal with a producer. The furnace is in effect a cylinder, mounted horizontally, and rotated slowly about a horizontal axis, the advantage being that a mixing action is obtained simultaneously with the melting which facilitates matters and improves the quality. The mounting enables the cylinder to be up-ended for the purpose of charging and discharging, the heat being applied as a jet inside the cylinder from one end. Reports indicate that the process is hard on linings, though the action should be uniform, and relining necessary only when the whole has worn through, in distinction to the selective action which takes place in stationary melters. An excellent method of relining these rotary melters is a one-piece effect produced by moulding the lining of pot clay to fit the drum, drying and firing it in the melter.

Pyrometers—*Temperature Measurement.*—The practical man can always gauge the temperature to within 50° C. by means of the eye, but this is scarcely satisfactory, since the required man may not be available, it is not accurate enough, and no record is obtained. The first instrument produced for temperature measurement above the range of the ordinary thermometer was the clay cone named after the inventor, Seger; it is a pyramid about 3 inches high composed of special clay mixtures having a definite softening point. A whole range of these exists for measuring temperatures from 600° C to 2,000° C. by 20° intervals, and in use the temperature has first to be judged roughly; then five cones of adjacent melting points are selected, the middle one agreeing with the estimated temperature. The five are stood erect in a fireclay holder and inserted in the furnace. If the first two cones should have collapsed, the middle one having commenced to deform, and the remaining two being unaffected, the true temperature agrees with the estimate. The cones may be placed in any part of the furnace, but if used much are expensive, and occasionally prove unreliable. Modern improvements include more compact designs.

These cones are not true measuring instruments, simply showing when a certain temperature has been passed, and belong to the class of instruments called pyroscopes. The actual measurement of temperature beyond the range of thermometers is undertaken by the instruments known as pyrometers. There are four commercial types of pyrometers, thermo-electric, radiation, resistance, and optical, the first three depending upon the relation between heat and an electric current passing through a wire. It is known that if two dissimilar wires are connected together to form a circuit capable of carrying an electric current, and that if one junction of the two wires is heated, an electric current is produced in the wires which increases with increased temperature (or rather increasing difference in temperature between the hot and cold junctions of the wires). This current can be measured by connecting the remote ends of the wires to a delicate milli-voltmeter. For furnace work, wires 2 feet long are used, covered by a case made of quartz, porcelain, or fireclay, and generally surrounded by an iron tube as a protection against oxidation and furnace fumes. The actual junction is placed in the furnace at any desired point, often through the roof, whereas in the case of the radiation pyrometer a more sensitive instrument is employed at a distance, the heat from the furnace being focussed on to a tiny junction of wires. For accurate work ‘ black body ’ conditions are necessary, which means using a point source of heat with no outside interference, though focussing on one article in an enamelling furnace provides a near enough approximation. Otherwise the temperature measurement is similar in principle to the thermo-electric pyrometer. The resistance pyrometer depends upon the physical law that the resistance of a wire to the passage of an electric current is proportional to its temperature, and in this case the wire in a sheath is inserted in the furnace and the resistance measured by suitable accurate instruments. The optical pyrometer depends on the measurement of the light which accompanies heat. Charts have been drawn up indicating the temperatures corresponding to colours, for example :—

First visible red = 450° C.
Cherry red = 750° C.
Orange = 950° C.
White = 1,200° C.

The optical pyrometer contains an accurately graduated scale of this type, and by viewing the furnace through a form of telescope, a match with this scale is made and the temperature recorded. The colour for matching is now generally produced by heating a filament by an electric current similar to an electric light globe. Apart from this the optical instrument has no association whatever with electricity. For accurate working by this method, ‘ black body ’ conditions are again necessary.

The thermo-electric method, like the resistance, measures the temperature of the furnace and not that of the actual article. It is suitable for all temperatures between 500° C. and 1,000° C. ; the radiation and optical instruments are particularly suited for higher temperatures, whilst the resistance method is intended for lower temperatures in the neighbourhood of 500° C. Since the thermo-electric and resistance pyrometers are quite automatic in action, permanent records of the temperature may be obtained. For these reasons the thermo-electric is generally the instrument selected. The cheapest pair of metals to employ is *iron-constantan,* which is only satisfactory up to 800° C. For temperatures up to 1,000° C., a junction of base metals (*Titan alloy*) is suitable, but for temperatures of 1,000° C. constantly, with occasional measurements of 1,200° C., a junction between platinum and an alloy of platinum, 90 per cent., and rhodium, 10 per cent., is advisable. Since the instrument actually measures the difference in temperature between the hot and cold junctions of the wires, care must be taken to maintain the latter as constant as possible. A degree or so is not material, and protection may be obtained by inserting the cold junction in about 2 feet of earth, or in oil, or by using one of the compensators sold for the purpose.

It is possible to have a battery of six thermo-electric pyrometers with one recording instrument in the manager's office which will show on his arrival in the morning the exact working of every furnace during the preceding night. Such an outfit complete costs about £120. The reading of the instruments may be easily checked either by immersion in boiling sulphur, or in the molten metals, all of which have definite fixed points, or by means of the instrument known as a potentiometer which is usually supplied with the instruments for the purpose of checking them.

Equipment for Fusing.—The equipment such as fire bars, spikes, and pettets to be employed must necessarily depend on the class of work to be handled, but the materials in general use are the same. Mild steel and wrought iron have been the standard materials in the past, but their obvious drawback is their failure to withstand the constant heating and cooling, leading to softening, the points blunting, and continual scaling with consequent damage to the ware, the furnace, and weakening of the bar until it becomes useless. Experience has shown the average life of a mild steel bar to be ten days. It has but one virtue, cheapness. Any attempt to alter the chemical composition of the steel is attended with appreciable increase in cost of the material, but progress has been made by the use of nickel and chromium alloys corresponding with the use of these materials for stainless steel, the requirements for both purposes being very similar, namely, resistance to oxidation. These nickel and chromium alloy bars are now available on the market under a variety of trade names, and though they cost ten or twenty times as much as mild steel, are cheaper in the long run by virtue of their long life. Their one limitation is a slight tendency to brittleness, requiring more careful handling than steel, though they are well capable of withstanding normal factory usage. Lightness and rigidity are the essentials in the construction of the fire bars, it often being overlooked that the weight is applied to them in only one direction, hence thin strips of good width are preferable to square section material, and the weight of steel may often be reduced without loss of strength by drilling holes in the bars. When similar loads are to be continuously fused, one rigid framework of bars to fit the furnace is preferable to a series of loose ones, and this arrangement applies more particularly to the spikes which come in contact with the ware.

The spikes must, of course, mark the ware as little as possible, hence they must be as sharp as possible, and with a little thoughtful arranging they may be reduced to an absolute minimum still retaining the article in shape. The use of irons and weights for straightening hollowware on its withdrawal from the furnace is barbaric but often necessary, and requires to be done with care. Many a good article has been ruined by straightening after it has cooled, causing cracks. Spikes are available in the special steels, though their brittleness counts against them, and the need is not so pressing.

Any reader further interested in the subject of refractories is again recommended to the works of A. B. Searle, particularly " Refractory Materials " (Griffin).

CHAPTER XI.

CAST IRON ENAMELLING.

CAST iron enamelling differs from steel enamelling in method rather than in principle, consequently most of the remarks appearing elsewhere apply equally well to either. Differences in execution are bound to arise, firstly, because of the different composition of the two metals and, secondly, owing to the greater thickness and weight of cast iron.

The enamelling of cast iron is an older industry than that dealing with steel, and though the latter has reduced the demand for cast iron domestic hollowware, the recent extensive housing schemes have created an enormous demand for cast iron baths and other fittings. In most respects the process is easier, since softer enamels are used, though furnace control needs to be keener, a uniform heat being essential, and any tendency to over-fire fatal.

Cast iron differs in composition from steel generally in that it is much less pure, or, in other words, that the foreign elements, carbon, phosphorus, silicon, sulphur, and manganese are present to a much greater extent, and, further, that these proportions are likely to vary considerably in different samples. When associated with a high percentage of certain metals, for instance, chromium, iron can dissolve large percentages of carbon, but the maximum solution of carbon in pure molten iron is 4·25 per cent. This solution on cooling deposits part of the carbon as such, the remainder being held in combination with the iron. The two are distinguished as graphitic carbon or graphite, and combined carbon. Cast iron containing no free graphite is known as white cast iron, and is hard and brittle. Ordinary foundry cast iron is grey iron, *i.e.*, containing free carbon, and may be distinguished by marking the fingers like a blacklead. This grey iron does not shrink as much as white on cooling and hence moulds better. Iron shares with water and one or two other materials the peculiarity of expanding at certain stages during cooling, and whereas white iron has only one such period, grey cast iron has three, after which it contracts regularly.

On treating cast iron with dilute acid, the combined carbon gives the unpleasant smelling gases which are noticeable, and in dilute nitric acid produces the brown solution which may be employed for estimating the amount of combined carbon present, the graphitic carbon on such treatment separating out as black specks. The strongest cast iron contains graphite, but in very fine proportions and very evenly distributed.

In steel, of course, all carbon is combined, and it is the graphite in cast iron which causes difficulties in enamelling, for on coming into contact with the oxides in the enamels, it will on the slightest provocation free the metal, and either carbon monoxide gas or carbon dioxide gas will be evolved, with consequent blistering. The total carbon present in cast iron is usually between 2 and 3·5 per cent., generally near the latter limit, of which 3 per cent. may be graphite and the other ½ per cent. combined. The mere presence of this amount of carbon and the other elements leads to the possibility of internal changes with consequent expansion and contraction under heat treatment, and consequent strains in the metal. On rapidly cooling cast iron the graphite fails to separate, yielding white iron.

The influence of the other elements on the quality of the iron depends upon their nature, on the amount present, and on the amount of the other impurities.

Silicon is invariably present, the proportion ranging from 0·5 to 4 per cent., generally between 1·5 and 2·5 per cent. being present. No element is of more interest to the foundry man. Silicon promotes the separation of graphite, itself combining with the iron, probably as Fe_2Si. High silicon irons are more expensive, but valuable in keeping sulphur low. Silicon was originally considered to be objectionable in any proportions, but is necessary to allow the iron to run when hot, and the addition of silicon to white iron increases strength and decreases shrinkage until graphite forms, after which shrinkage increases. Silicon varies in proportion from pig to pig.

Sulphur is objectionable as it gives a white cast iron which is brittle and weak. For foundry practice the proportion should not exceed 0·15 per cent., and still less is advisable for enamelling purposes. Fortunately, in working about 95 per cent. passes into the slag, so that unless working is being carried out at low temperatures and with acid slags, a very high proportion of sulphur in the ore must be present to affect the iron materially. Sulphur, though generally very evenly distributed, may vary in different portions of the pig.

Phosphorus.—The principal influence of phosphorus is the production of very fluid metal. When in the neighbourhood of 0·55 per cent., excellent results are obtained, but 1·0 to 1·5 per cent. may be allowed if fluidity and softness are required, but proportions above 1 per cent. produce brittleness, and produce weakness more than any other element. It has no influence on changing white iron to grey or *vice versâ*, but is excellent for reducing blow holes, and it also reduces shrinkage. The phosphorus is combined with the iron, and the compound is so distinct that it is readily recognised and the proportion present may be estimated under the microscope.

Manganese.—This element is always present though it alloys and forms a solid solution with iron, and therefore cannot be distinguished under the microscope. It is usually present in proportions which do not materially affect the properties of the iron, though from 0·5 to 2·0 per cent. gives tenacity, and increases shrinkage. Its principal service is in counteracting the sulphur content, eliminating this element, for which purpose it is necessary in steel, and incidentally it also neutralises the effects of silicon. The addition of small proportions of ferro-manganese before pouring into moulds reduces the combined carbon by half.

Other possible elements include aluminium, chromium, arsenic, copper, titanium, vanadium and nickel, though they are not likely to be present in proportions which will interfere with the iron, but only traces of aluminium are necessary to convert combined carbon to graphite.

Pig iron is generally graded as follows :—

1. Open-grained Grey
2. Foundry
3. Forge
4. Mottled
5. White

Combined Carbon and Sulphur Increasing ↓

↑ Silicon Increasing

The following compositions of cast iron may be given—

TABLE XV.

	Grünwald	Staley	Ramsden	Typical Analyses		
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Combined carbon, .	. .	. .	0·63	0·14	0·28	0·75
Graphite, . .	. .	. .	3·05	3·54	3·01	2·50
Silicon, . .	2·0	1·5–2·5	2·66	2·80	2·55	1·95
Phosphorus, . .	1·4–1·8	0·5–0·6	0·72	0·75	0·70	0·30
Sulphur, . .	. .	0·04–0·08	0·05	0·01	0·02	0·02
Manganese, . .	0·5–0·7	0·4–0·6	0·59	0·30	0·40	0·53

A typical grey foundry iron is illustrated in Chapter I.

The enameller's attitude towards the composition of the cast iron may depend on whether or not the castings are made in the factory or are bought outside. In the latter case it would be difficult for him to draw up a definite analysis for a specification and more difficult to find anyone to supply it. He is more likely to have recourse to the favourite requirement "suitable for enamelling," which means little but a desire for a minimum content of graphite. In the event of trouble arising later the discussion turns upon whether it is the foundry man's duty to supply an iron to suit the enamel, or the enameller's business to use an enamel suitable to the iron. Foundry practice demands a mixture that will be fluid hot, and free from blowholes and slag, the last two requirements being equally necessary to the enameller. Hence it may be put broadly that cast iron which is satisfactory in the foundry can be enamelled, though naturally exceptions may arise under special circumstances. It is impossible commercially, however, to regulate the composition of cast iron as in the case of steel, and consequently variations arise which account for the greater number of rejects in enamelling which may be attributed to the metal base.

Castings for enamelling require to be as uniform as possible and as free from thickened portions, and sharp corners, as is practicable. Further, all facings for the moulds should be eliminated. It has been mentioned in Chapter VI. that if the expansion of steel be taken as 400, enamels are in the neighbourhood of 300, and this latter figure is approximately that for cast iron, hence the greater probability of crazing with cast iron enamels. The expansion of cast iron varies somewhat with composition, harder samples (*i.e.*, low in silicon and high in sulphur) have a higher expansion.

Whether or not it is an advantage to anneal the castings before enamelling depends somewhat on the enamel being used. Annealing should lessen the likelihood of cracks appearing after enamelling, but cast iron on heating to 700° C. undergoes a permanent increase in size, which is mainly attributed to the silicon being oxidised to silica, hence once the casting has been through this treatment the contraction in cooling is greater than during the first operation, consequently annealed castings need an enamel with a higher expansion. Whether annealing is practised or not, consistency is the essential point, for if some samples are annealed and others not, and the same enamel used for both, troubles will result. Castings are almost invariably cleaned by sand blasting, a mixture of sand and steel shot being recommended. The articles to be blasted are contained in an air-tight cupboard or room, according to size, and the sand forced by air pressure in a fine spray against the object. The workers need protection for the parts of their bodies likely to become exposed, and altogether the work is not of a pleasant nature. The sand is recovered after use, sieved, and the serviceable material used again. The best practice is to anneal first, then blast, followed by a second short annealing. No time should be lost between cleaning and applying the first coat of enamel.

Methods of Enamelling Cast Iron.—The two distinct methods of enamelling cast iron are the dry process, which consists of dusting the powdered enamel on to the heated casting, and the wet process which with one distinction, is the same as in the steel process. The choice of method for applying the enamel will depend mainly on the size, shape and weight of the casting to be treated. Large and uneven objects, including baths, are enamelled by the older dry process, whilst the increased business in stove parts and similar flat and regular castings has given a fillip to the newer wet process. The means of carrying out the two methods may be compared roughly with the obsolete and modern methods of steel enamelling. Wet processes fail on irregular castings because a cold coated object placed in a furnace will not attain a uniform surface temperature in the same time, owing to the varying thicknesses of metal, in consequence of which the enamel will be either underfired on the thick portions or burnt out on the thinner sections. In the dry process, of course, this is obviated by waiting until the casting is uniformly heated before applying the enamel. In the case of both processes a distinction may be drawn between the use of enamels containing lead compounds, and those which are leadless, though this makes no difference whatever to the method of application. Another modification is where distinct ground coats are abandoned, though in the best practice they are retained in both methods.

Considering the dry process first, the chief characteristic here is that a very thin ground coat is applied, followed by two or more thick cover coats. The composition of the ground coat is not of the outstanding importance as in the case of steel; it is applied in the same manner but very much thinner in consistency. The quickest available method of application is employed, generally by painting on with a brush, or the complete immersion of the article, followed by draining. In composition this enamel is very often of the same recipe as the subsequent cover coats, but it is melted and ground wet in the same way as steel ground coats except that a smaller proportion of clay and a larger proportion of water are used at the mill. A typical recipe reads :—

Borax, ...	32 per cent.
Felspar, ...	64 „
Red lead, ...	4 „
	100 „

On grinding, 1 per cent. clay added.

When the coated casting is dry, it is gradually warmed on a flue or in a furnace maintained especially for the purpose, as in the case of baths. It is then transferred to the fusing furnace and the ground coat thoroughly burnt in, until the casting attains the same temperature as the furnace. No thickness of enamel is perceptible, and the coating is so thin that it can scarcely be described as either glossy or matt, its function being to prevent any action between the carbon in the iron and the subsequent cover coat of enamel. Firing-in the ground coat requires ten to thirty minutes, when the casting is withdrawn and the powdered cover enamel dusted on through sieves as evenly as possible, the article being returned to the muffle for a few minutes to fuse the enamel, then withdrawn and the process repeated. Since the whole process must be completed at one attempt, skilled judgment is necessary in determining the number of dustings to be given. Generally two are sufficient, though large articles may have four or even five. To allow to cool down and then reheat, in addition to being expensive is distinctly risky, a large proportion of the articles being broken in the process.

The actual enamel is melted in identical fashion to steel enamels, splintered in water, and the frit thoroughly dried. It is then ground dry with about an equal weight of stones until the enamel will no longer grit between the fingers, tin oxide and often zinc oxide having been added before grinding. Excessive care is necessary to exclude dust, and it is advisable to treat the powder enamel with a magnet, since dry grinding is a slower process, and harder on the mill lining. Subsequent treatment consists in repeated sieving to remove foreign matter and oversize material.

Enamels melting at much lower temperatures than steel enamels are employed, and this softness, together with a high lustre, were at one time universally produced by the aid of lead compounds. With the gradual elimination of this material from glazes in pottery work, similar progress has been made in enamels for dusting, and perfectly satisfactory white enamels are made without its use. For coloured enamels, the majolica finish obtained with lead enamels, cannot be reproduced without its aid, though leadless coloured enamels are being developed. The ground coat need contain no cobalt, though small percentages are sometimes retained for traditional reasons. A simple mixture from such ingredients as borax, nitrate, felspar, and quartz is all that is required, though where lead is used high proportions of nitrate are essential. Since high proportions of borax and zinc oxide are common, the enamel is very fluid when molten, and runs like water, hence devitrification has to be guarded against, and for this reason, tin oxide is sometimes fluxed with the frit, though such a procedure is expensive.

An example of a lead and leadless cover coat follow, the first being due to Riddle (*Trans. Amer. Cer. Soc.*, IX., p. 646).

Lead Enamel.

Barium Carbonate, ...	11·1	per cent.
Borax, ...	14·2	,,
Calcium Carbonate, ...	3·4	,,
Felspar, ...	30·5	,,
Lead Oxide, ...	20·7	,,
Soda, ...	4·5	,,
Sodium Nitrate, ...	3·0	,,
Tin Oxide, ...	11·1	,,
Zinc Oxide, ...	1·5	,,
	100·0	,,

The leadless enamel reads :—

Borax,	51·3 per cent.
Cryolite,	10·2 ,,
Felspar,	35·9 ,,
Soda,	2·1 ,,
Sodium Nitrate,	0·5 ,,
	100·0 ,,

On milling 12½ per cent. of tin oxide is added.

The analyses of these two enamels read :—

Na_2O,	6·5 per cent.	16·3 per cent.
K_2O,	5·9 ,,	6·9 ,,
CaO,	2·4 ,,	—
BaO,	9·7 ,,	—
PbO,	23·4 ,,	—
ZnO,	1·7 ,,	—
Al_2O_3,	6·4 ,,	10·3 ,,
SiO_2,	25·4 ,,	26·7 ,,
B_2O_3,	5·9 ,,	21·3 ,,
F_2,	—	4·2 ,,
SnO_2,	12·6 ,,	14·3 ,,
	100·0 ,,	100·0 ,,

or, expressed as molecular formulæ :—

Na_2O, 0·25	$Al_2O_3 = 0·15$	$SiO_2 = 1·0$
K_2O, 0·15		$B_2O_3 = 0·2$
CaO, 0·15		$SnO_2 = 0·2$
BaO, 0·15		1·4
PbO, 0·25		
ZnO, 0·05		
1·00		

and

Na_2O, 0·810	$Al_2O_3 = 0·190$	$SiO_2 = 1·088$
K_2O, 0·190		$B_2O_3 = 0·824$
1·000		$F_2 = 0·294$
		$SnO_2 = 0·250$
		2·456

Riddle gives the following limits for a powder enamel :—

F_2, .	less than 0·135
Ba, .	. up to 0·45
B_2O_3,	. 0·05–0·30
PbO, .	. 0·1–0·4 (excess of PbO gives yellow enamel).
Al_2O_3,	. 0·1–0·25
SiO_2, .	. 0·75–1·25

The following limits are given by Shaw (*Trans. Amer. Cer. Soc.*, XI., p. 103) :—

Na_2O,	0·80	$Al_2O_3 = 0·36$	SiO_2,	0·516
K_2O,	0·19		B_2O_3,	0·420
MgO,	0·01		F_2,	0·990
			SnO_2,	0·160
	1·00			2·086

and

Na_2O,	0·832	$Al_2O_3 = 0·273$	SiO_2,	1·040
K_2O,	0·156		B_2O_3,	0·572
MgO,	0·012		F_2,	0·819
			SnO_2,	0·322
	1·000			2·753

The Wet Process.—If the method for steel enamelling is retained in its entirety, failure results owing to the poor adherence of the ground coat. Glossy ground coats are unsatisfactory and the composition adopted is a mixture of ingredients of a more refractory nature than usual, and instead of complete melting this mixture is subjected to muffle temperature (800° to 900° C.) in clayed pots for a few hours. This burns off all volatile matter, melts the fluxes, and produces a sintered mass, which when applied correctly to the iron looks as though it might be rubbed off with the finger, though actually it should resist scraping with a knife. The sintered mass is broken up, ground with clay and water, and applied like a steel ground coat, though, since the majority of pieces will be too heavy to dip, spraying is a more common means of application. The "frit" often represents only 50 per cent., or even less, of the ground coat enamel, refractories such as clay or flint being added to render the mass harder. A leadless mixture for such an enamel reads :—

Borax,	27·6	per cent.
Quartz,	69·0	,,
Soda,	3·4	,,
	100·0	,,

On grinding, Quartz added = 33·3 per cent.
,, Clay added = 10·0 ,,

The analysis of this enamel reads :—

Na_2O,	5·35	per cent.
Al_2O_3,	2·76	,,
SiO_2,	83·50	,,
B_2O_3,	8·39	,,
	100·00	,,

and the molecular formula is :—

$Na_2O = 1·000$ $Al_2O_3 = 0·348$ $SiO_2 = 15·30$
$B_2O_3 = 1·26$
$16·56$

A lead ground coat due to Danielson and Reinecker * reads :—

Borax,	29·5	per cent.
Boric Acid,	5·7	,,
Flint,	55·9	,,
Red Lead,	3·3	,,
Sodium Nitrate,	5·6	,,
	100·0	,,

On grinding, 15 per cent. Clay is added.

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* "Wet Process Enamels for Cast Iron."

The analysis reading :—

Na_2O =	5·46	per cent.
PbO =	3·66	,,
Al_2O_3 =	5·26	,,
SiO_2 =	69·70	,,
B_2O_3 =	15·92	,,
	100·00	,,

and the molecular formula being :—

$Na_2O = 0{\cdot}885$
$PbO = 0{\cdot}115$
1·000

$Al_2O_3 = 0{\cdot}346$

$SiO_2 = 7{\cdot}38$
$B_2O_3 = 1{\cdot}57$
8·95

One or two cover coats are next applied very thinly, as in steel enamelling, each successive coat being dried, warmed and then fused. Coloured enamels may be successfully applied without a ground coat. The compositions of a lead and leadless white cover coat follow. Lead is still largely retained in wet, cast iron enamels, particularly in American practice. It is difficult to report on the position in this country since little headway has been made with the wet process.

Lead Enamel.

Borax,	19·2	per cent.
Felspar,	8·0	,,
White Lead,	12·0	,,
Quartz,	28·0	,,
Soda,	8·8	,,
Sodium Nitrate,	8·0	,,
Tin Oxide,	8·0	,,
Zinc Oxide,	8·0	,,
	100·0	,,

On grinding, Clay added = 7 per cent.
,, Tin Oxide added = 4 per cent.

Leadless Enamel.

Borax,	39·5 per cent.
Cryolite,	13·2 ,,
Felspar,	39·5 ,,
Soda,	2·6 ,,
Sodium Nitrate,	2·0 ,,
Tin Oxide,	3·2 ,,
	100·0 ,,

On grinding, 7 per cent. Clay is added.
,, 7 ,, Tin Oxide is added.

The analyses read :—

	Lead.	*Leadless.*
Na_2O,	12·65 per cent.	16·16 per cent.
K_2O,	1·51 ,,	7·41 ,,
PbO,	12·00 ,,	—
ZnO,	8·99 ,,	—
Al_2O_3,	4·15 ,,	14·05 ,,
SiO_2,	40·20 ,,	31·33 ,,
B_2O_3,	7·88 ,,	16·01 ,,
F_2,	—	5·30 ,,
SnO_2,	12·62 ,,	9·74 ,,

and the molecular formulæ :—

$Na_2O = 0·521$	$Al_2O_3 = 0·041$	$SiO_2 = 1·382$
$K_2O = 0·041$		$B_2O_3 = 0·302$
$ZnO = 0·302$		$SnO_2 = 0·150$
$PbO = 0·136$		1·834
1·000		

Na_2O, 0·780	$Al_2O_3 = 0·315$	SiO_2, 1·815
K_2O, 0·220		B_2O_3, 0·660
1·000		F_2, 0·420
		SnO_2, 0·180
		3·075

The handling of cast iron ware for enamelling lends itself more readily to mechanical treatment, or rather mechanical means are more often essential to this class of work. In the case of household baths, overhead cranes and runways are essential, together with a turntable mechanically operated for rotating the bath through all angles when withdrawn from the furnace for dusting. The dusting is usually conducted through sieve boxes operated by electricity or compressed air to produce the necessary vibration.

CHAPTER XII.

THE FACTORY LAY-OUT.

WHILST an enamelling factory should conform to most of the accepted ideas on factory construction, like every other industry it has its peculiarities. Perhaps first in importance under this heading is the large area required per head employed. During the drying operations, every article requires stacking individually with space around it to permit of air circulation, and as the wet enamelled article does not permit of transport such as elevation to a higher floor a large ground area is necessary. Further, the article has to occupy this space for some hours until it is dry. Enamel factories vary in architecture as a galvanised chapel varies from a cathedral, and what may be an undreamed of luxury to the one is a trifling necessity to the other, consequently many of the facilities mentioned in this chapter will be quite beyond the resources of the smaller man.

The one-floor factory is to be favoured throughout with the exception of the enamel preparing department, and possibly the warehouse. Good lofty buildings are a necessity, with good natural and artificial lighting, since the work generally continues the twenty-four hours round, and close inspection is necessary to detect faults during the progressive stages of manufacture. The advisability of working continuously has been called into question repeatedly owing to the loss of quality and output which occurs during the night hours, and some works have abandoned the 10 p.m. till 6 a.m. night shift owing to the inability to get satisfactory supervision. The argument applies also to the melting of the enamels, but as both types of furnace suffer by continual raising and lowering of temperature, together with the increased overhead charges on a smaller output, continuous working is still the general practice.

Dust being the great enemy of the enameller, special precautions are necessary for its exclusion. Wherever external doors exist double doors are advisable, as these help to prevent dust and draughts simultaneously. The atmosphere should be uniform and warm. The means of providing heat are already present, and it will probably be necessary to remove heat more frequently than to provide it. Overhead fans achieve this, and may be assisted by the more modern means of suction through gratings on the floor level. By these means dust is removed at the same time. All possible facilities should be provided for keeping the workpeople and the work-rooms scrupulously clean, since success depends on this so largely. The actual disposition of the buildings will depend mainly on the available site, the most suitable disposition having the buildings with their long sides parallel and close together, or in hollow square formation, or a combination of the two arrangements.

The bulkiness of the commodity being manufactured emphasises the necessity of a railway siding to a works of anything above a modest output, and as this will also be the means of admittance of coal and raw materials, it must be considered very seriously in conjunction with the layout of the works. Where export work is undertaken, proximity to a canal is useful. Transport within the factory calls for good organisation. General practice relies entirely, and all enamellers depend to a greater or less extent upon hand labour in this direction. This may be partially replaced by conveyors of the endless belt type, and electric hoists and runways, but the difficulty is to obtain a sufficiently smooth action to eliminate the risk of damage to the ware. American practice favours the mono-rail and all forms of overhead runways. At some stages recourse must be made to the trolley, man operated, and it is here that an efficient organisation will ensure that the most suitable of the many ingenious devices available are employed. In this connection the floor material comes in for consideration, and a hard wood surface apart from the immediate vicinity of the furnaces has much to recommend it, one point in its favour being the lesser damage it inflicts upon accidentally dropped ware.

The cleaning or pickling department is one which readily lends itself to automatic and semi-automatic transport facilities. It should certainly be housed in a separate building and the fumes excluded from the enamelling department. All fittings require to be rendered acid-resisting, either by their material of construction or by liberal painting. The pickling department is generally associated with the enamel preparing department, and under the one control. By the use of resistant material for making crates, the incoming steel blanks should require no handling between grease burning and examination prior to enamelling. This is made possible by the use of monel metal, a compound mainly of copper and nickel; its physical properties are such as to permit of its being cast and worked into suitable containers for the steel shapes, and its chemical properties permit its being immersed in the acid as a whole and removed by means of an overhead runway to the washing and neutralising tanks. From these the crate may be deposited into a steam heated conveyor and delivered to a suitable spot for examination and distribution to the dippers. The idea may be carried a stage further where spinning and stamping operations are conducted at the enamelling factory. Articles, particularly small ones such as lids, which are fiddling to handle, may be dropped direct from the machine in a monel metal basket, and not subsequently handled until the examining stage is reached, and may be weighed as many times as is necessary *en route* by means of an overhead weighing machine. A claim has been made that monel metal baskets facilitate pickling owing to the electrolytic effect of having the two different metals (the monel metal and the steel blank) immersed in the same acid solution. An overhead weighing machine useful in the pickling department and in the mill room, made by Messrs. Avery, Ltd., is illustrated in Fig. 18.

Every owner of a factory would presumably desire his roof to be weather proof, and it is therefore superfluous, perhaps, to make any observation on the matter here, but as a leaky roof causes endless damage to work so largely distributed, special reference to this feature may be justified. No industry can depend for its existence more than enamelling does upon the quality of labour employed. The process is dependent from first to last upon human judgment and skill. The limitations of mechanical transport have been mentioned, and though pyrometers in the furnaces facilitate control, success still depends on the workman's judgment. The method of applying enamel by means of a spraying apparatus is quite familiar and has been mentioned previously, but it is in no sense an automatic method, depending entirely on the operator's skill. Mechanical means should be adopted whenever possible, however, for in addition to the obvious advantage of accuracy and regularity, they save floor space and set a pace for the workman.

Apart from the enamel ingredients, the main materials required are water, coal, and iron, and the availability of

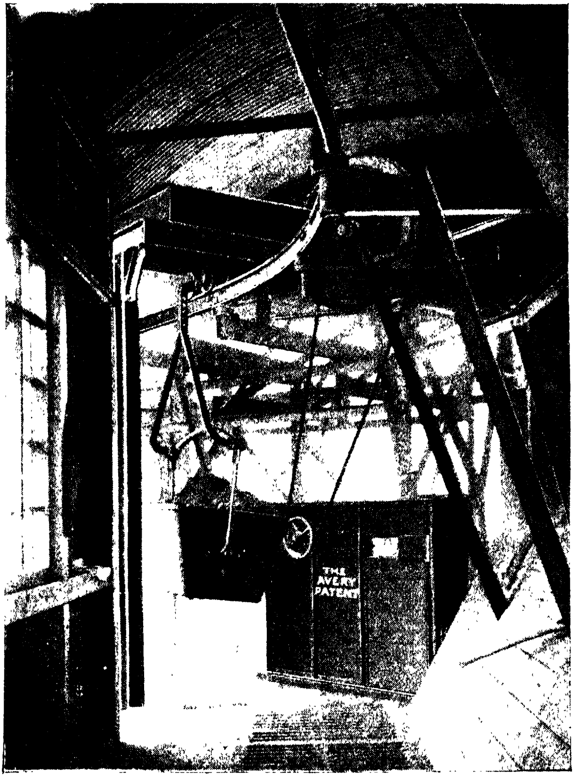

Fig. 18. Patent Automatic Overhead Weigher and Totaliser (Avery).

these generally determines the situation of the works. Water is available everywhere, but varies in quality, the softest water possible being the best for enamelling purposes for the reasons previously given. The raw materials for enamel manufacture are drawn from all corners of the world, and do not vary much in price from one end of the country to the other, the factories therefore generally follow the coal and iron mines, and the industry in England has established itself in the Midlands, the most notable exception being the largest hollowware factory in South Wales.

Another issue affecting the geographical situation is whether it is proposed to manufacture or to buy the steel blanks for enamelling. The obvious advantage of the former is that it gives control of the process practically from the source, enabling models especially suitable for enamelling to be made, exclusive designs to be introduced, and eliminates the necessity of carrying a large stock of blanks. On the other hand the plant for stamping and spinning will require a very large proportion of the available capital, and possibly the output may not justify this running continuously at full pressure. Further, the public fancy is very fickle, requiring new designs frequently, and the manufacturer may be left with useless dies and presses. In the Midland area, competition is keen among metal stampers and spinners, who work not only for enamellers but japanners, tin men and galvanisers, so that prices are keen and the advisability of buying the blanks may be considered, and the devoting of the capital thereby released to equipping and organising an enamel shop embodying really modern facilities. Spinners making for the other trades, however, often offer the enameller an atrocity suffering from every conceivable fault, such as different gauged parts, semi-open seams, wired beads, heavy seams, loose joints and riveted parts, which are not so objectionable to the other trades. As an illustration, Fig. 19 shows two types of bead on a kettle neck, the first is satisfactory for enamelling, the second not, because the enamel collects under the bead, where it cannot be removed and forms lumps or blisters. Where the capital is available to justify the machinery department these difficulties are overcome, but the plant must be exploited to the full, surplus output being sold, otherwise manufacture cannot be competitive. The stipulation mentioned regarding the large area of ground space per man employed applies also to the stamping department where the shells cannot be economically stacked. When stamping is undertaken it is a short and highly desirable step to introduce rolling mills to produce one's own steel and ensure a uniform material, and thus attain another stage in the control of the process.

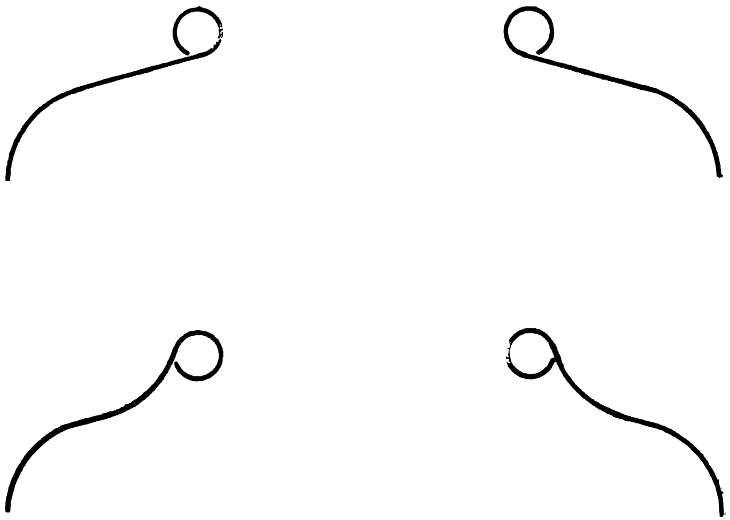

Fig. 19.—Two Types of Bead on Necks of Kettles.

It may seem anomalous in times of industrial depression to say that the enamelling industry is short of the desired labour, but this may influence the choice of the factory site. In Germany, it is traditional that son succeeds father in foremen's and similar responsible positions. Here the system is insufficiently old to permit of such a system, but the family connection is quite strong and it may be necessary to place the factory where the labour exists.

Any system of organisation must originate from the muffle furnace. There must be sufficient work to justify keeping at least one furnace continuously occupied for six days a week, this then becomes the unit of output and all other departments must be manned to provide and deal with this output. The size of plant, number of dippers and warehousemen, and all details will vary enormously with each class of work handled, but the labour required for each operation in any particular plant should be definitely known, and consequently any tendency to overstaff readily detected. For efficient control an adequate recording system is essential, and it requires but a small portion of a clerk's time to show the progress of each department daily. A simple chart of this nature immediately points to a weakness and prevents particular items being unduly delayed at any stage, at the same time showing the exact state of the factory daily. Many enamellers are essentially 'practical' men, with a fine scorn for figures and papers, in consequence of which they work in the dark regarding actual costs. An adequate costing system, accurately worked out, is more essential in a cut-price industry, such as enamelling, than in the more protected trades allowing liberal profits.

Few will dispute the advisability of a general introduction of the piece-work payment system, since few industries lend themselves to it so readily as enamelling.

A variety of ways exists for fixing rates according to value, weight, size, or number of articles produced. Where fusing is being considered, so much per load is a solution for routine work, but where a variety exists recourse is often made to a weight basis. The main objection is the extra supervision required to ensure the smaller work being fired in turn and not left for the next man to do. A modified system of a price based on weight multiplied by count overcomes this objection. For the actual enamelling a count is the usual basis of payment. When two different systems are employed under the same management, it is not immediately obvious that the output of one department agrees with the intake of the next; for example, one hundred thousand articles may be dipped and forty tons fired during the same period, when the relationship is not very obvious. The system of weighing should be as limited as possible as the article is varying in weight throughout manufacture, and on reaching the warehouse will eventually be sold on a count. When weighing is employed two sets of scales should be employed, so that the output from one department may be checked against the intake of the next. Incidentally, where wages are paid on a weight basis, the scales must be open to the inspection of the local Weights and Measures department.

APPENDIX.

TABLE XVI.

CONVERSION OF ° C. TO ° F., AND ° F. TO ° C.

° C.	° F.	° C.	° F.	° F.	° C.	° F.	° C.
0	32	350	662	0	−18	850	454
5	41	400	752	10	−12·5	900	482
10	50	450	840	20	−7	950	510
15	59	500	932	30	−1·5	1,000	538
20	68	550	1,020	40	4	1,050	565
25	77	600	1,112	50	10	1,100	593
30	86	650	1,203	60	15·5	1,150	621
35	95	700	1,292	70	21	1,200	649
40	104	750	1,382	80	27	1,250	676
45	113	800	1,472	90	32	1,300	704
50	122	850	1,562	100	38	1,350	732
55	131	900	1,652	150	66	1,400	760
60	140	950	1,742	200	93	1,450	788
65	149	1,000	1,832	250	121	1,500	816
70	158	1,050	1,922	300	149	1,550	843
75	167	1,100	2,012	350	177	1,600	871
80	176	1,150	2,102	400	204	1,650	899
85	185	1,200	2,192	450	232	1,700	927
90	194	1,250	2,282	500	260	1,750	954
95	203	1,300	2,372	550	288	1,800	982
100	212	1,350	2,462	600	316	1,850	1,010
150	302	1,400	2,552	650	343	1,900	1,038
200	392	1,450	2,642	700	371	1,950	1,065
250	480	1,500	2,732	750	399	2,000	1,093
300	572	1,550	2,822	800	427	2,050	1,121

General Rule.

$$^\circ\text{C.} \times 1\tfrac{4}{5} + 32 = {}^\circ\text{F.}$$

$$^\circ\text{F.} - 32 \div 1\tfrac{4}{5} = {}^\circ\text{C.}$$

TABLE XVII.

CONVERSION OF CENTIMETRES TO INCHES AND INCHES TO CENTIMETRES.

Centimetres.	Inches.	Inches.	Centimetres.
0·1	0·04	$\frac{1}{16}$	0·159
0·2	0·08	$\frac{1}{8}$	0·318
0·3	0·12	$\frac{1}{4}$	0·635
0·4	0·16	$\frac{3}{8}$	0·953
0·5	0·20	$\frac{1}{2}$	1·270
0·6	0·24	$\frac{5}{8}$	1·587
0·7	0·27	$\frac{3}{4}$	1·905
0·8	0·31	$\frac{7}{8}$	2·222
0·9	0·35	1	2·540
1	0·39	0·1	0·254
2	0·79	0·2	0·508
3	1·18	0·3	0·762
4	1·58	0·4	1·016
5	1·97	0·5	1·270
6	2·36	0·6	1·524
7	2·76	0·7	1·780
8	3·15	0·8	2·032
9	3·55	0·9	2·29
10	3·94	2·0	5·08
15	5·91	3	7·60
20	7·87	4	10·16
25	9·84	5	12·7
30	11·81	6	15·2
35	13·78	7	17·8
40	15·75	8	20·3
45	17·72	9	22·9
50	19·69	10	25·4
60	23·62	11	27·9
75	29·53	12 = 1 Foot.	30·5
100	39·37	36 = 1 Yard.	91·4

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