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ALIZARINE,

NATURAL AND ARTIFICIAL.

FRED. VERSMANN, PH.D.

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New York, November, 1872.

My Dear Lutz,

The discovery of artificial Alizarine created at the time a most profound sensation, it realized the chemist's wish and dream, so long indulged in, to rival nature's skill in the production of a most lovely and most useful color.

What seemed to be almost impossible but four years ago, has become a plain matter of fact to-day; as soon as the direction had been pointed out, it was at once followed up, and now this valuable color is manufactured by the ton as a regular article of commerce.

You were among the first, who realized the importance of this new production, and who foresaw the revolution, it is sure to create in one of the largest industries of this large country.

You were the first to import from Germany this last and brightest child of, what in the highest meaning of the word is called, "*applied chemistry.*"

Is it therefore surprising that you should wish to find a home for this German child here, where everybody is welcome, who possesses health and strength and vitality. And of these sterling qualities the new comer has plenty, and he will show them, before he is much older; but at the present moment he is young and may want some one to vouch for his good qualities and to place them in the proper light.

Hence it is very natural, you should have expressed the desire of placing before your business friends a short account of this new discovery, which will enable them to judge for themselves of the advantages in printing and dyeing with artificial Alizarine, instead of with Madder, advantages which are sure, sooner or later, to induce the consumers to adopt the one and to discard the other.

I have been fortunate in my visit to America, inasmuch as it gave me an opportunity of learning your wish, and of trying to comply with it myself. I have written a short account on Alizarine, natural and artificial, comprising the principal facts, which I thought would interest your friends, and I offer them to you with the earnest request to accept the same as a token of my sincere friendship. With these feelings I inscribe the following pages to you and I remain, my dear friend,

Yours Very Truly,

FRED. VERSMANN.

Louis Lutz, Esq.,
Messrs. Rumpff & Lutz,
42 Beaver St., New York.

ALIZARINE,

NATURAL AND ARTIFICIAL.

NOTHING IS LOST IN NATURE!

This is merely another expression of the grand truth, that matter is indestructible, and the sentence conveys one of the most cheering lessons, the attentive study of natural sciences and especially of chemistry teaches us every day.

Wonderful as have been the discoveries of chemistry during the last five and twenty years and astonishing as have been the results of these discoveries when applied to art and manufacture, they are in no way more beneficial than in bringing out the truth of the motto: Nothing is lost in Nature.

In turning scientific investigations to practical account there will often be a tendency to look at the ultimate result only, but the higher lessons which every new discovery carries along with it, cannot be overlooked by the lover of nature and of science, and if in the following pages an attempt be made to describe the latest triumph of scientific research, it will surely not be out of place to draw attention to this noble undercurrent. And it will be easy to do so by tracing back our subject to its origin.

Artificial Alizarine, this beautiful coloring substance, is manufactured from Anthracene, which in its turn is obtained as a bye-product in the manufacture of gas from coal, but where does the coal come from and how is it formed before we find it in the ground?

The answer to this question we may find to some extent by looking at the constant changes around us, and by studying the wonderful effect the sun has upon vegetation and the different ways this effect makes itself visible.

The seed buried in the fruitful ground is called to life by the genial warmth of the soil, and as soon as it shows above ground it is further developed into a sapling and into a tree by the heat and light-yielding rays of the sun; these assist and facilitate the assimilation of nutritive salts from the soil and of carbonic

acid from the air, the component parts of which form the body and substance of the tree.

Now let us look at the various colors of the leaves, flowers and fruits, all so much condensed sunshine, as it were, absorbed and stored up by the different parts of the tree. With the change of the seasons we see these colors pass through various shades, all indicating changes of the highest importance, which have been attentively studied, although not yet fully disclosed. But we know that the change in color of the leaves from the refreshing green in spring to the beautiful red and yellow in autumn and ultimately to the sombre brown of the dead leaves is owing to chemical changes, assisted, if not produced, by the light and heat of the sun.

No wonder this subject has been studied by many men of science, especially since the use of the spectroscope has opened up a new field of investigation and has revealed new distinctive marks of substance which chemical analysis does not disclose. Sorby has published an interesting paper on the various tints of autumnal foliage, in which he gives the results of his investigations by the spectroscope; he distinguishes more than twenty coloring matters, which he places in several groups such as bright green, representing complete vitality and growth, red and scarlet, indicating low vitality and change, and dull brown, signalising death and decomposition. He justly observes that the fine tints of autumn are indications of the diminished vital powers of the plants, an observation which is strengthened by the fact of unhealthy branches of a tree turning yellow while the rest remains green.

How sad the idea that all the beautiful life of one season should delight us for so short a time only and should then be lost for ever! How grand, how lofty on the other hand the conviction that *nothing is lost in Nature* and that every thing will reappear again and again in due time, although in different forms.

The seed grows into a mighty tree, which forms only a single unit in a forest, but let such forest by some violent revolution in nature be buried deep beneath the ground, covered perhaps mountain high by rock and soil, and let it rest there for generations, hidden from the light, until man's industry and

perseverance traces it and brings it forth, not in the shape of trees but in the form of solid, massive blocks and seams of coal.

The tree, from a chemical point of view, consists chiefly of carbon, oxygen, hydrogen and nitrogen in a variety of combinations, and slow, indeed, must have been the process of separating the carbon in the form of black coal, and fearfully strong must have been the pressure of the rocks around and above, to condense the gaseous oxygen and hydrogen in this carbon.

Having thus attempted to trace the origin of coal, I may go a step further and glance at its application for the production of gas, and thereby indicate that the heat and light absorbed by the tree during its growth and life is set free again and utilized. Coals heated in a closed vessel yield so many products of decomposition, gaseous, liquid and solid, that their investigation has been a fertile field for chemical research, for many years. The general development of gas industry is highly interesting, because in no other direction has the advance in science been of greater service.

Gas has become such absolute necessity now a days, that we can scarcely realize all the difficulties, all the prejudices which had to be overcome in the introduction of this substitute for the sun.

When not quite sixty years ago, the idea was first originated in London, to light up some streets with gas, and for that purpose to erect a gasholder and store a quantity of gas, the whole undertaking appeared to be so utopian, even to scientific men, that Sir Humphry Davy suggested, the inventors of this wonderful discovery might perhaps convert the large dome of St. Paul's cathedral into a gasholder.

About the same time, Mr. Ackermann, of the Strand, in London, was the first to erect a small gas retort in connection with his kitchen range, and the gas thus obtained, without any previous purification, was burned in the shop. This novelty was so astonishing, that a lady of title offered Mr. Ackermann ten guineas for his new lamp, which she was anxious to take home in her carriage, and very angry she grew indeed, on learning that the lamp was a fixture and could not be used without a certain apparatus in the kitchen.

When, a few years later, the House of Parliament was to be lighted with gas, the members became so afraid of the heat conveyed through the pipes, which they expected to be filled with fire, that they insisted upon having the pipes several feet away from the walls of the building, so that these might not be injured by the great heat given off by the pipes.

These anecdotes show how little people understood the nature of gas when first introduced, and in like manner chemists formerly were ignorant of the nature and of the component parts of gas.

To-day it is well understood, that next to the solid carbon in the coal the compressed and condensed hydrogen is of the greatest importance in the gas manufacture; this element partly combines with carbon to a series of compounds which are called hydrocarbons; these burn but do not emit a clear, brilliant light, because they are too rich in carbon; a large amount of hydrogen, however, passes into the gas not combined with carbon or any other element and serves to dilute and carry along the heavier hydrocarbons, thus giving a mixture suited for lighting purposes.

Before leaving the gas works, the gas must be deprived of a variety of impurities, one of the most important of which is tar. This uninviting, unpleasant and for a long time unprofitable article has become the special subject of chemical investigation and has risen to very great importance.

Nearly fifty years ago, in 1825, Faraday obtained Benzole from coal tar, but many years passed before a practical application of this hydrocarbon was originated by Perkin, who first succeeded, in 1856, in manufacturing from Benzole a variety of those splendid colors, generally known under the name of Aniline dyes or colors. Tempting as is the subject of these dyes, I must pass it by here, remarking only that they afford the first demonstration of the return, or the resurrection of those beautiful colors of the leaves, flowers and fruits spoken of before, and which had been buried in the coal for ages. The manufacture of these Aniline colors, differing from all previously known colors, has assumed enormous dimensions during the last fifteen years, and has most materially in-

fluenced not only the commerce, but also the taste and fashions of the whole world.

The astounding scientific and commercial results obtained in this direction, gave certainly a mighty impulse to further investigations on the part of many chemists of all countries, which finally culminated in the production of artificial Alizarine, another beautiful coal tar color, the special subject of these pages.

The success of artificially producing this color is of the utmost importance, not only because the substance thus produced is destined to supplant one of the most ancient and fastest colors ever known or because its introduction will have a marked influence upon the agricultural aspect of several countries, or again, because mighty industries have sprung up and will spring up in consequence of this discovery, but chiefly and most prominently because the artificial building up in the laboratory of Alizarine is the first instance of a faithful reproduction of an organic dye.

The discovery of Aniline dyes was the discovery of an entirely new range of chemical compounds endowed with those beautiful colors, none of which had ever been known before; the discovery of the process of artificially making Alizarine, is of the highest scientific interest; it results in the formation of a substance known and used for centuries, but hitherto produced by the hand of nature only. And as success has crowned the chemist's labors in one direction, so surely will other imitations of Nature's work be triumphantly carried out. To-day we manufacture Alizarine; when shall we manufacture Indigo? The solution of this problem is a mere question of time, but come it must, and to judge from certain indications, in no distant time.

If I wish to speak of artificial Alizarine, its preparation and its qualities, I must of necessity refer to the substance it is destined to supplant and to supersede, and it will be more convenient to do so here. I will therefore give a short outline of the history of madder colors and then pass on to the artificial compound.

MADDER AND COLORS DERIVED FROM IT.

The plant which yields madder root is called Madder in English, Krapp or Faerberroethe in German, Garance in French, Alizari in Greek and Italian; the botanical name is Rubia tinctorum; the red coloring matter is not found in the whole root but almost entirely in the outer part, the inner or woody part yielding scarcely any coloring matter at all.

The coloring matter is not ready formed in the outer part of the root. Decaisne and Koechlin have shown that the coloring matter in the fresh root is yellow and becomes red under the oxydising influence of the air; this same process of oxydation takes place to a certain extent when the roots are left in the ground for several years; and this loss of time is naturally one of the greatest disadvantages of Madder cultivation and the cause of a slow and unsatisfactory return.

In France the roots are left in the ground for two or three years, in Turkey and the East five and more years; in the eastern countries the roots are merely dried in the open air and then exported without further preparation, while in France and Holland the roots are first artificially dried and then ground to powder.

But even then the Madder is not ready for immediate use, but is kept for another two or three years, when the coloring or dyeing strength is much improved. This of course is owing to chemical changes, which formerly were but little understood, and as, with prolonged keeping for years, these changes go on till the coloring power is seriously injured or almost destroyed, the article requires much care and attention.

Much uncertainty and risk is thus involved in the cultivation of Madder; a crop which can only be gathered in at the end of two or three years, and which even then is not ready for immediate use and which, while growing, is subject sometimes to complete failure, is a very dangerous and unsatisfactory return for the capital and labor invested in its production.

The growth of madder has been confined to a few countries, foremost among which stand France, Holland, Italy, Turkey

and southern Russia, but interesting experiments for its cultivation have been made in other countries. The soil, the climate and the weather have the most decided influence upon the growth of the plant and the subsequent developement of the coloring principle. Thus, Dutch madder will dye red, but not purple, and the color is not fast, Naples madder from Italy dyes good red and purple, but the colors are not fast, that from Turkey dyes good reds and purples and is very fast. France supplies the market with two qualities, called rosées, from their dyeing beautiful reds and pinks, and paluds, the last name being given because the roots are grown on marshy land; this gives a good purple, besides fine reds and is the best French quality.

Mr. T. Sidebotham has published the results of some interesting experiments on the cultivation of madder-roots, made some years ago in England. A piece of rich land in Derbyshire was sown with seed from fine palud madder, early in the spring of 1868, in the autumn the madder plant came into flower and the roots of some pulled up measured thirteen inches. The plants came up in the spring of 1869 very strong and healthy and so on until August, 1871, when they were dug up. To produce the best results, the roots should have remained another year in the ground, but for experimental purposes this growth was considered sufficient. The quantity produced was small, in appearance and size the roots were about equal to fine French roots, but on breaking them, instead of the deep red color in the best French roots, they were orange or yellow.

The dyeing properties were of a very disappointing character, the colors after soaping were loose and similar to Dutch Madder, pinks and reds being loose and weak and the purple element entirely wanting; the deficiency of coloring matter may be owing to want of sun and heat. It is said that French seed, grown in Holland, does not produce a French quality, but one similar in every way to the usual Dutch Madder.

These results show most conclusively the effect of the soil and climate, and it is to be hoped that Mr. Sidebotham has put aside and intends to keep for some years, part of his crop

in order to learn whether or not a chemical change and consequent improvement in the coloring matter will take place.

The whole question has for many years been enveloped in mystery and uncertainty; at the present time, however, we know that Madder contains chiefly two coloring principles, *Purpurine* and *Alizarine*, which may be separately obtained and applied. As stated before, these colors are not ready formed in the roots, but are products of decomposition of another substance, which has no coloring property; according to Decaisne's microscopical investigations, the fresh roots are filled with a yellow transparent fluid, which turns red under the influence of the air after the cells are broken.

The subject of extracting the coloring principles has occupied many people, and has become the subject of many patents in various countries. The more foreign matter is mixed up with any color, the more the latter must lose in brilliancy and purity, and many attempts have been made to concentrate the coloring matter of Madder, but the preparation of pure or nearly pure Purpurine and Alizarine is of recent date. It would be out of place to record all the different methods proposed in the manufacture of Madder preparations, but a short account of the more important ones must not be omitted.

For many centuries and until the beginning of the present one the root itself was applied directly, and without any scientific principle. Schunck was the first, in 1851, to study the change in the root, he separated a peculiar ferment and a substance named by him *Rubian*, which by the action of the ferment is converted into Alizarine. He also observed that weak acids had the same effect, an observation which some years afterwards found practical application.

The analysis of Madder root shows that it leaves about 20 per cent. of dry substance, but the commercial article contains from 16 to 18 per cent. of moisture.

100 parts of the dry root contain:

Substance soluble in cold water,	55·0 parts.
" " " boiling water, (including most of the color.)	3·0 "
Substance soluble in alcohol,	1·5 "
Fibrous matter,	40·8 "

Among the substances soluble in water are gum, sugar, pectic acid and a yellow coloring matter, discovered by Kuhlmann in 1824, and called by him *Xanthine*, but which has not found practical application. The solutions in boiling water and alcohol contain chiefly resins and coloring matter.

The amount of sugar is considerable, some ten or fifteen per cent., which is converted by some French manufacturers into alcohol; Madder is washed with water, the washings are allowed to ferment and the alcohol thus formed is distilled off; a ton of Madder gives about thirty gallons of alcohol, which has a peculiar, unpleasant flavor, but it is well adapted for technical purposes. It has also been suggested to dissolve the sugar and to separate it as such; this idea might possibly be practically carried out, if the cultivation of Madder carried with it the promise of a long life.

Schutzenberger's complete analyses of Madder and its different preparations are also of interest, in as much as they show the inorganic impurities contained in the color.

Name of substance.	Inorganic substance or ashes, of which	Soluble in water, chiefly chloride of potassium, little carbonate of lime.	Insoluble in water, viz.	Silica.	Carbonate of lime.	Phosphate of lime.	Sulphate of lime.
Avignon madder.	13·63	3·00	10·63	2·90	5·72	1·93	
Flowers of madder. (Fleur de garance.)	12·63	0 77	11·85	3·28	6·24	1·70	
Garancine.	17·75		17·75	10·20	4·48	1·90	1·06
Alizarine, commercial	11·80		11·80	8·14	2·58	1·03	
Madder carmine.	12·00		12·00	4·50	5·50	trace.	1·95

Originally Madder was used without any preparations, merely dried and kept a sufficiently long time to develop the coloring substance; but attention was directed to the removal of some of the foreign matter, which led to the manufacture of *fleur de garance*, which is simply madder deprived of all substances soluble in water and afterwards dried again. Then the manufacture of *garancine* was commenced in 1839; this is

Madder still more concentrated by treatment with sulphuric acid, which destroys part of the woody fibre ; after that *extracts of Madder* were introduced, and finally *commercial Alizarine and Purpurine*, the two coloring principles separately and in a pretty high state of purity.

Julian and Roquet were the first to introduce a purified article, which they called "*fleur de garance*," and theirs is still a very important article of commerce in France ; they merely extract the substances soluble in water and dry the residue, amounting to about 60 per cent. of the Madder used ; the aqueous solution containing all the sugar, is allowed to ferment and the alcohol thus formed, separated by distillation, as before mentioned.

Robiquet and Collins observed that sulphuric acid does not destroy the coloring matter, and Lagier and Thomas produced, in 1839, an article, the manufacture of which is based upon this observation ; they named their product "*Garancine*." Madder is boiled with Sulphuric acid for some hours, the liquid is separated by filtration, the residue washed with weak solution of Carbonate of Soda, to neutralize any acid, pressed and dried, 100 parts of Madder yield from 35 to 37 parts of Garancine. in the form of a fine powder, of a light brown color, which is four times as strong as Madder.

Pincoff and Schunck introduced the application of steam in the process of washing; the madder loses much more in quantity, but the quality is greatly improved.

These and other methods had advanced but little the progress in the preparation of a pure article, when Kopp published his investigations, the result of which was the direct application of Schunck's previous observation as to the action of weak acids, and on Kopp's plan the manufacture of much purer articles was undertaken by Schaaf and Lauth, at Strassburg, who have now for years brought their preparations into the market. This is the most decided practical advance in the history of Madder, and a short account of the process may be found interesting.

Large wooden tanks with false bottoms are charged with 600 lbs. of ground Madder and 1000 gallons of sulphurous

acid water at the time. The mixture is allowed to stand for 12 hours, when the liquid is drawn off through a tap at the bottom; the residue is washed with another 150 gallons of acid water and the liquid run off after a couple of hours and mixed with the first, these liquids are filled into the Purpurine vats, holding about 1500 gallons each; three per cent. of sulphuric acid are then added and the whole heated by steam to about 35° to 40° C., when Purpurine soon begins to separate in large flakes; after 12 hours' standing the Purpurine is collected on a filter, washed with water and dried; the colored liquid is drawn off into the Alizarine vats, then heated to the boiling point, when an impure substance, called green Alizarine, separates, which is collected similarly to the Purpurine.

100 parts of Alsatian Madder yield ½ to ⅔ per cent. of Purpurine, which is about 20 times as powerful as Madder, and 3 per cent. of Alizarine about 20 times as strong as Madder. The Madder residue is not fully exhausted, but is treated with the acid washings from Alizarine and dried; the products, about one third of the original substance, is similar to garancine but is only half as strong. But even then another preparation is obtained from the washings of the last operation; these are kept for some time, when a brownish Alizarine separates, which is collected and sold as an extract, being from 1 to 1½ per cent. of the Madder first taken.

Purpurine is little soluble in acid water, pretty soluble in pure water, it is freely taken up by solutions of alumina salts, gives very pure red, pink and black shades; dilute Iron mordant does not produce purple, but rather dark, grayish brown shades. Purpurine colors are not acted upon even by direct sunlight, but they are not proof against hot soap solutions, this disadvantage becomes less serious by the fact that the shades are very bright and that the goods require only to be passed through weak soap solutions, to have the white ground restored. 15 to 20 grains are sufficient to dye a square yard of mordanted cloth, even with heavy designs.

Green Alizarine (*alizarine verte*), has all the properties of flowers of Madder, the color produced is just as fine but faster; its intensity is not impaired by soap, acids, alkalies or tin solu-

tions, on the contrary, the color becomes brighter; the mordant must be one eighth to one tenth weaker than with flowers of Madder. Boiled with concentrated hydrochloric acid, green Alizarine scarcely loses in weight, but it then dyes purple and lilac with a purity and brightness which surpasses any other Madder preparation.

Yellow Alizarine. In treating green Alizarine with alcohol, 20 to 30 per cent. of yellow Alizarine are obtained, and in this manner the first alcoholic extract was prepared, the direct treatment of flowers of madder or garancine with alcohol, offering too many practical difficulties. Kopp afterwards substituted schiste oil or petroleum as cheaper and better suited for the purpose.

1 part of green Alizarine is boiled with 15 to 20 parts of rectified petroleum boiling at about 150° C., as soon as the boiling ceases, the green insoluble matter separates as a sediment, after a few minutes the liquid is decanted, it contains much Alizarine, part of which separates on cooling; as soon as the liquid has cooled down to about 100° C., dilute caustic soda lye is added and the mixture well shaken. The lye takes up all the Alizarine with a blueish purple color, while the petroleum becomes almost colorless and may be used again. The lye is then poured into dilute sulphuric acid, Alizarine separates in yellow flakes, which are collected on a filter, washed until perfectly free from acid and dried. This yellow Alizarine then is the purest article of commerce and from it absolutely pure Alizarine may easily be obtained by sublimation. Robiquet and Colin, of Paris, were the first to separate it from Madder as far back as 1826; they treated Madder with strong sulphuric acid and charred most of the fibrous substance, from the resulting black mass called by them charbon de garance, they obtained crystals of pure Alizarine by sublimation.

Another process, which has been followed very extensively and for many years, is based upon Leitenberger's observation that the two coloring principles are separately soluble in water at different temperatures, viz.: that Purpurine is soluble in water at from 25° to 55° C., while Alizarine requires a very

high temperature. Leitenberger therefore repeatedly extracts Madder with water heated by steam to a temperature not exceeding 55° C. and precipitates the Purpurine thus dissolved by Lime or Barytes; the precipitate is then decomposed by hydrochloric acid, when the Purpurine separates; it is then washed and dried.

The Madder is afterwards dried and fully exhausted with boiling wood-spirit, which dissolves the Alizarine, this is separated nearly chemically pure, by pouring the solution in water. According to Leitenberger's statements he obtains 2 to 3 per cent. of Purpurine and 4 to 4½ per cent. of Alizarine, he also claims great superiority of his preparations over other products, which he has expressed in the following numbers, as quantities required to produce the same effect upon equal pieces of cloth:

Leitenberger's Alizarine,	2
Schaaf and Lauth "	8
Garancine,	20
Madder,	70 to 80

Extracts of Madder, are prepared by many firms, amongst whom Pernod holds a prominent position, he thinks extracts of Madder ought to be used like extracts of logwood and other dyewoods by printing directly and steaming without the use of a mordant and that the cause of frequent failure is owing to the great impurity of most extracts. He therefore produced an extract which is in fact a mixture of coloring matter and a mordant. He treats Madder or better Garancine with boiling water until all the coloring matter is exhausted; on cooling an orange colored precipitate separates, which is collected on a filter, washed, thickened with gum or starch and according to the shade required acetate of Alumina or of Iron added; this extract is ready for printing, the goods are steamed and passed through a soap solution at 60° C.

This extract contains 10 per cent. of dry residue, it is four times as strong as good flowers of madder, and superior to it in brightness and purity of shade.

Before leaving the subject of treating madder I may mention another process which is based upon the very opposite principle of that followed in all other methods. All other manipula-

tions aim at the extraction of the coloring matter from the woody fibre, leaving the last undissolved, while Paraf, the inventor of this new process, proposes to remove the great bulk of the fibre by a solvent, which does not act upon Purpurine and Alizarine; his idea is to treat madder with an ammoniacal solution of oxide of copper which shall dissolve the fibre, while the coloring substances form an insoluble compound with the copper which is then separated. The idea certainly claims the merit of novelty, but the expenses involved in the process must make its practical application more than questionable.

Purpurine and Alizarine are then the two important principles in Madder, but others of minor importance have also been separated, and to complete the description I will subjoin a table giving the names and properties of all those coloring principles in Madder, which have occupied the attention of many chemists.

Name.	Spectroscope.	Crystallization.	Effect of heat.	Solubility in		
				Alkalies.	Benzole.	Alcohol.
Alizarine.	Band near red	Long orange colored needles.	Readily sublimates.	Blueish purple solution.	Soluble.	Soluble, more readily in warm than cold.
Purpurine.	One band near red, another near yellow.	Red needles, sublimated and then crystallised from alcohol.	Sublimates under decomposition.	Red solution.	Soluble.	Same as above.
Pseudopurpurine.	Same as above.	Fine brick red needles crystallised from benzole.		Red solution.	Soluble.	Very little soluble.
Orange matter.	No bands.	Small groups crystallised from alcohol.	Decomposes and yields purpurine.	Red solution.	Insoluble.	Readily soluble.
Purpurosanthine.	No bands.	Yellow needles. crystallised from alcohol and benzole.	Sublimates.	Yellow solution.	Soluble.	Soluble.

Alizarine sublimates at a temperature of about 240° C. and may then be collected as pale orange crystals; it is nearly insoluble in water, but the solubility increases with the temperature, viz.:

100	parts	of	water	of 100 ° C.	dissolve	·034 parts.
"	"	"	"	150 "	"	·035 "
"	"	"	"	200 "	"	·820 "
"	"	"	"	225 "	"	1·700 "
"	"	"	"	250 "	"	3·160 "

The above five substances are closely allied in chemical composition, and this similarity strengthens Decaisne's opinion, that the Madder root originally contains only one color-giving principle, which by the oxidising influence of the air is successively converted into Alizarine, Purpurine and the other compounds. Bolley showed that Purpurine heated to a high temperature loses oxygen, and is converted into Alizarine.

As all Madder preparations have frequently been adulterated, it may be useful to state a simple method of testing their purity. Pernod divides the dyewoods and other substances which may be used for this purpose into two classes, namely, those which give colored combinations with alumina and iron, such as brazilwood, logwood, fustic, etc., and those which contain tannic acid, but no coloring principles, or at least very little, such as several barks, galls, sumac, etc. The last do not produce any colored combination with Alumina, while they give black or brown precipitates with oxide of iron.

To detect even small quantities of any of the substance belonging to the first division, the following test is given; take a piece of white paper about four inches square, dip it into an acid solution of chloride of tin, place it on a glass or porcelain plate and sprinkle a little of the finely powdered substance over it. In about half an hour any adulteration will show thus: brazilwood carmine red points; logwood purple spots; fustic yellow coloration, while with pure Madder only a faint yellow color will show. The same method is followed in looking for substances of the second class, merely substituting a solution of sulphate of iron for the chloride of tin. Any substance containing Tannic acid will produce blueish black spots, which increase in intensity the more the sample is adulterated. One part of any of such fraudulent admixtures in a thousand part of Madder may thus readily be detected.

ARTIFICIAL ALIZARINE.

Anthracene $C_{14}H_{10}$.

The substance which serves as the starting point of the manufacture of artificial Alizarine, is Anthracene, one of the many hydrocarbons obtained in the distillation of coal tar. This substance, *Anthracene* is, as its name indicates, a derivative from coal, viz. ἄνθραξ coal. In distilling coal tar, the first portion of distillation contains Benzole, the liquid hydrocarbon, discovered by Faraday, and which is the basis of the Aniline colors, while the very last portions of this distillation yields the solid hydrocarbon Anthracene.

Both Benzole and Anthracene were known to chemists for many years before the great practical importance they enjoy to-day became evident, but there is a radical difference in the manner in which they were introduced into technical industry, which may be well worth while to point out.

In looking at the development of any industry, or at the practical application of scientific discoveries generally, we mostly find that the starting point, i. e. the raw material which serves as the basis of some new chemical compound, has been well known for years and it may be, that its very abundance has suggested some new application. This was very likely the case with Benzole, and its investigation first undertaken by Perkin, which ultimately resulted in the production of the Aniline dyes. Very seldom indeed, has a substance been taken out of the collection of interesting but practically useless chemical compounds and has suddenly become a most important article of manufacture and commerce. Such however, has been the case with Anthracene, which was commercially unknown at the time when the process of converting it into Alizarine was first discovered, until then, only three years ago, perhaps not 10 lbs. had ever been separated, while to-day it is manufactured in very large quantities.

Anthracene was not commercially known before its present application; true it was obtained in the distillation of coal tar, the last portions of which are used in England as a good lubricating material under the name of *green grease*, but the

buyers of this article often complained to the distillers of a *sediment or grit* in the oil, which they returned as useless and which of course, was chiefly the now valuable Anthracene.

Dumas and Laurent, in 1832, first obtained Anthracene from the last fractions of the distillation of coal-tar; the oily matter was exposed to extreme cold, when a crystalline substance separated, which was pressed and treated with alcohol, and the residue was further purified by redistillation, crystallization, and sublimation. This product, however, was not pure Anthracene, as shown by the low melting point of 180° C. and by the formula assigned to it, viz.: $C_{15}H_{12}$, which is half as much again as that of Naphthaline, for which reason the authors named the new hydrocarbon Paranaphthaline.

Laurent submitted the compound to new investigations, and obtained several interesting derivatives, but as Professor Kopp suggests, in his masterly memoir on Anthracene and its derivatives, published in the *Moniteur Scientifique*, Laurent had evidently only small quantities of the impure hydrocarbon at his disposal, and he therefore, could not determine the true composition of the substance, which he now named Anthracene.

Fritsche, in 1857, described a hydrocarbon obtained from coal-tar which he found closely to resemble Anthracene, but which had a melting point of 210—212°C. and gave the formula $C_{14}H_{10}$.

Anderson published in 1862 a most searching investigation on Anthracene and its derivatives; he retained Laurent's name of Anthracene, and confirmed Fritsche's formula $C_{14}H_{10}$.

Limprecht showed, in 1866, the production of Anthracene from the decomposition of chloride of Benzoyl by water, at 180°C.; and in the same year Bertholet commenced his splendid researches on the action of heat upon the hydrocarbons, their origin, characters, and composition; he showed the circumstances under which Anthracene is formed by the action of heat upon several more simple hydrocarbons; he found that Toluol, or mixtures of Styrol and Benzol, of Benzol and Ethylene, passed through a red hot tube, furnished Anthracene; he also described the extraction of Anthracene

from coal-tar, its purification and character, and further confirmed Anderson's results.

In 1867 Graebe and Liebermann commenced their valuable publications on Anthracene, Anthrachinon and artificial Alizarine, which have now become the starting point of a new and most important branch of industry in England and in Germany.

Although the artificial production of Anthracene has been indicated by Bertholet, there is no likelihood of its ever being successfully carried out on a large scale, and coal-tar will always remain the basis of Anthracene manufacture.

In distilling coal-tar the last 10 or 15 per cent. of the product of distillation are collected separately, and are allowed to stand for some time, when a crystalline deposit of solid hydrocarbons separates, which is freed from adhering oil by filtration and pressing. But the quantity thus obtained is only small, if compared with the large demand; as soon as Graebe and Liebermann's process of converting Anthracene into Alizarine was shown to be practicable and highly remunerative, other chemists brought out different processes, all of which have been patented in Europe, and the demand for Anthracene rapidly increased; it is, therefore, not surprising to find that the price of *pure* Anthracene in Europe has risen within two years from £50 a ton to £500, and even more.

It is also natural, that chemists and manufacturers should have tried to discover new sources of this valuable substance. Now in distilling coal-tar the residue in the still is pitch, and it has hitherto been assumed, that all the Anthracene could be extracted by the old process. Fenner and Versmann, however, were the first to discover and to practically demonstrate that much more Anthracene could be obtained by continuing the operation, with increased heat, until the pitch has been completely destroyed or converted into coke.

Their invention, which has been protected by letters patent, both in this country and in Europe, consists in obtaining Anthracene from pitch as a separate operation, and in the combination of this process with the ordinary method of

distilling coal-tar, by which a considerable portion of Anthracene is saved, which otherwise would be lost.

The product obtained in either way, is mixed with a considerable quantity of heavy or dead oil, from which it is separated, as already stated, by filtration and pressing; the residue in the form of a more or less dry cake of greenish yellow color, contains from 30 to 60 per cent. of pure Anthracene, and forms the ordinary article of commerce, which is sold by percentage of the pure substance.

The impurities of this article are chiefly dead oil and two other solid Hydrocarbons, Naphthalene and Chrysene, and as the manufacturers of Alizarine require a nearly pure substance, they are very anxious to induce the tar distillers to supply them with an article as pure as possible. Dr. Gessert, one of the earliest and most successful manufacturers of Alizarine, writes on this point, as follows: It is to be regretted that the tar distillers are not more careful in the manufacture of commercial Anthracene. The manufacturer of Alizarine has not the necessary plant at his disposal, which is required for the purification of such impure Anthracene; at all events he loses much time, and has no use for the oily residues resulting from the purification.

The tar distillers on the other hand, can always use their by-products along with their other oils; they ought to take the greatest care in the pressing of the well-filtered and drained Anthracene, by using powerful hydraulic presses, and by pressing first cold and then hot, as strongly as possible. Such crude, well-pressed Anthracene is readily powdered and passed through a sieve, and in this state of fine division it may be treated with petroleum spirit, boiling between 70° and 90°C. and after sufficient washing, it may again be submitted to strong pressure.

The percentage of Anthracene depends upon the quality of coal, and it differs with coals from different localities. It is generally assumed that the coal which yields much Benzole gives also much Anthracene, while coals producing a tar rich in hydrocarbons of a higher boiling point, such as Toluol, Xylol and Cymol, contain but little Anthracene. In

England it is stated that Glasgow and Edinburgh tar, which yield little Benzole and much Toluol is poor in Anthracene, and that the tar from South Staffordshire coal is rich both in Benzole and Anthracene.

This distinction may possibly hold good in the separation of Anthracene from coal tar only, but it loses its importance when pitch is operated upon, because there is little doubt that while the Anthracene is ready formed in the tar, it is not so in the pitch, but it is a product of decomposition resulting from the effect of increased heat.

The average quantity obtained from the distillation of coal tar is about half a per cent., whereas in Fenner and Versmann's process the pitch yields about two per cent. of Anthracene. A valuable by-product in operating upon the pitch is the coke, which is of course quite free from sulphur and so dense as to withstand the strongest blast; for this reason it is well adapted for smelting purposes and is as good as wood charcoal in the manufacture of steel.

This new process of manufacturing Anthracene is of great importance, inasmuch as the yield from coal tar altogether is increased about five times, and serious doubts as to the possibility of meeting the demand have thereby been effectively removed. It may therefore be interesting to learn, that one of the patentees, the writer of these pages, is at present in this country with the view of introducing the new process, and that he has already succeeded in starting large works, so that in a short time Anthracene will be added to the list of articles of export to Europe.

The commercial Anthracene is not pure, but contains, according to the care and attention paid to its manufacture, from 30 to 60 per cent. of pure substance. It is sold by percentage of pure Anthracene, to ascertain which, a uniform test is employed.

A given quantity of the sample to be analyzed is boiled with alcohol, the same relative proportion of both always being taken; it is then allowed to cool, placed on a filter washed with another quantity of alcohol, dried and weighed; an additional test is made by determining the melting and

solidifying point, which should be as near as possible to 210°C. (410°F).

The commercial Anthracene is further purified by washing with light petroleum spirit, it is then sufficiently pure for manufacturing purposes, but it is by no means chemically pure and to obtain it in this state is a rather tedious process, a detailed description of which would be out of place here.

Pure Anthracene crystallizes in rhomboidal plates, which melt at 213°C. (415°F) to a clear colorless liquid, which soon becomes colored. On cooling it assumes the appearance of a foliated, crystalline mass. It distils at about 360°C. (680°F) and this quality is sometimes taken advantage of in its purification. The partially purified material is placed into a retort and heated to the melting point; a current of air is then blown into the retort; the Anthracene is rapidly carried off and solidifies in the neck of the retort in the shape of brilliant flakes with a beautiful violet fluorescence.

It is very indifferent to most solvents, cold Alcohol, Benzole and Bisulphide of Carbon dissolve ·6, ·9 and 1·7 per cent. respectively, considerably more when hot; it is insoluble in water and solutions of caustic alkalies, sulphuric acid, even when concentrated, dissolves Anthracene, without decomposing it, but it forms compound acids; light petroleum, which readily dissolves Naphthalene, has but little effect upon Anthracene, but the heavy oils of coal tar and petroleum dissolve it in considerable quantity, and the separation is often, especially in hot weather, a matter of some difficulty.

Picric acid forms a very remarkable compound with Anthracene, viz., Picrate of Anthracene, which may serve to characterize the Hydrocarbon and to distinguish it from Naphthalene and other homologous Hydrocarbons. On mixing boiling alcoholic solutions of Picric acid and of Anthracene the Picrate deposits on cooling in the form of fine starlike needles, of a very brilliant ruby red color, appearing as long prisms under the microscope.

Artificial Alizarine. $C_{14}H_8O_4$.

Alizarine obtained from Madder has often been analyzed by chemists, and it may be, that the different results obtained as to its chemical composition, owing to the difficulty of preparing it absolutely pure, may have somewhat retarded the solution of the great question, how to obtain it artificially.

After the wonderful success of the Aniline colors, all derived from coal tar, it would have been very natural to search amongst the substances derived from the same source for one, which properly treated, might yield Alizarine. But the number of chemical compounds, which have already been separated from coal tar, is so large, that the task of submitting even a part of them to investigation with the object of obtaining a certain result would have been entirely hopeless.

Instead of trying, therefore, to obtain Alizarine from some other substance, two German chemists, Messrs. Graebe and Liebermann conceived the idea of taking Alizarine from Madder and endeavoring to split it up into more simple compounds, and in this they succeeded; they obtained Anthracene from Alizarine, after which it was a comparatively easy task to convert Anthracene into Alizarine.

The discovery is scarcely three years old, but its vast importance became evident at once to many people, and to-day we see five or six large firms in Germany and England manufacturing this new color every day by the ton.

A detailed consideration of the scientific chemical part of the manufacture would lead me too far away; suffice it, therefore, to say that Anthracene is not directly converted into Alizarine in one single operation, but an intermediate compound, Anthrachinon, ($C_{14}H_8O_2$) is first formed, from which Alizarine is obtained.

Graebe and Liebermann, Gutzkow and Brunner and Perkin are patentees of several processes which differ but slightly; they vary only in the modus operandi and in the chemicals employed, but the result of all their manipulations is always the same, viz., the conversion of Anthracene into

Anthrachinon and then into Alizarine; this is expressed by the following formula:

Anthracene.	Anthrachinon.	Alizarine.
$C_{14}H_{10}$	$C_{14}H_8O_2$	$C_{14}H_6O_4$

According to Graebe and Liebermann's patent, one part, by weight, of Anthracene is heated for several hours with four parts by weight, of Sulphuric acid, sp. gr. 1848, at a temperature of about 100°C. (212°F.) and then for one hour at 150°C. (300°F.) After cooling, the mass is diluted with three parts of water and then two or three parts of Peroxide of Manganese are added; the whole mixture is boiled for some time, to complete the reaction the mixture may be concentrated by evaporation or may even be brought to dryness. Cream of lime is then added in excess to neutralize Sulphuric acid and to precipitate soluble Manganese salts and to the filtrate, Carbonate of Soda is added to separate any Lime. The clear liquid is evaporated to dryness, the saline cake thus obtained, is dissolved in water together with two or three parts of caustic Potash or Soda and heated for about an hour, at a temperature of from 180° to 260°C. (360°F. to 500°F.) until a sample dissolved in water gives a copious precipitate of Alizarine on addition of some acid. The whole is dissolved in water, acid is added in excess and the precipitate which is formed, is collected on a filter and well washed. Instead of Peroxide of Manganese other oxidizing agents may be taken, as for instance, Peroxide of Lead, Chromic acid, Nitric acid, etc. The precipitate thus collected and washed may be dried, when it represents the Alizarine in the most concentrated form, as a dry powder; but in practice it has been found to be more convenient to use it in the form of a paste and as such it is sold by all manufacturers. Most of the paste is brought into the market as containing 10 per cent. of coloring matter, seldom 12 per cent. The dry powder is not so readily dissolved or mixed in printing as the paste, and if the percentage of the last is to be depended upon, and if the inorganic salts are all removed by continued washing, the paste will be more acceptable to the printer than the powder.

I have made a series of experiments with samples from

different manufacturers in order to ascertain how far these conditions are complied with, and I give the result in the following tables:

I.	II.	III.	IV.	V.	VI.	VII.
			Solid residue consists of		Solid residue consists of	
	Per cent. stated.	Solid Residue dried at 120°6.	Organic Matter destroyed by ignition.	Inorganic matter less after ignition.	Organic matter insoluble in water.	Inorganic matter soluble in water.
No. 1.	10 %	10·64 %	10·53 %	·11 %	10·46 %	·18 %
2.	10	9·91 "	9·81 "	·10 "	9·76 "	·15 "
3.	10	9·99 "	9·48 "	·51 "	9·50 "	·49 "
4.	10	10·83 "	10·29 "	·54 "	10·03 "	·80 "
5.	10	22·89 "	?	? "	11·83 "	11·06 "
6.	12	12·38 "	11·75 "	·63 "	11·64 "	·74 "
7.	12	14·67 "	11·71 "	2·96 "	11·62 "	3·05 "

The third column gives the total amount of solid residue, which is separated in columns IV and V into organic matter and incombustible inorganic salts, and in columns VI and VII into organic matter insoluble in water and inorganic salts. Taking for a moment the organic matter of columns IV and VI as pure Alizarine, we find that all the samples contain nearly the amount claimed, while columns V and VII show that five of the samples are singularly free from inorganic impurity, that is to say have been well washed, while No. 7 is imperfectly washed and No. 5 is extremely impure. The last sample was, in every respect, the worst and differed from the others in every respect; the color of the differenpastes, with the exception of No 5, was of a greenish, olive brown to a bright yellow brown. The impurities in the samt ples were chiefly Potash and Soda, combined with Chlorine and Sulphuric acid. The Paste readily separated and the water above was nearly clear and colorless. No. 5 was of a dirty mud color, it smelled strongly of Acetic acid, the supernatant liquid was of a dark purple color, showing some of the Alizarine had been dissolved in free Acetic acid. The impurities, amounting to nearly the same weight of the organic matter, were chiefly Acetates, and for this reason the determinations of columns IV and V have not been given, as the residue left after burning, did not represent the original saline

impurities, the acetate having been decomposed by the heat. into carbonate.

Now comes the question whether the organic matter contained in the paste is absolutely pure Alizarine, and this question must at present, be answered in the negative. The transformation of Anthracene has not taken place without the formation of other products of decomposition, which may be carried into the precipitate. This is shown by heating some of the dried residue in a retort, when with all samples a carbonaceous residue was left in the retort, which would not have been the case, if all the organic matter had been pure Alizarine.

Schunck separated from artificial Alizarine a compound crystallizing in yellow, silky needles, which he named Anthraflavic acid; this substance is found to possess no tinctorial power; it cannot influence or weaken the effect produced by Alizarine. It is, of course, very desirable to obtain the substance as nearly pure as possible, and the manufacturers will, no doubt, very shortly succeed in doing so.

A much more important question than the absolute purity of the article is its identity with Alizarine from Madder, which, although proved to exist by many chemists, has been questioned by others. Bolley, Kopp, Schunck, Perkin and others, whose names are well known in connection with this particular branch of science, have come to the conclusion, that the chemical composition of the two substances is identically the same. Alfraise, a French chemist has, on the other hand, published experiments, made with the view to prove that the new preparation is not Alizarine, but Bolley insists that these experiments were not made with sufficient care and with too impure a material, to deserve the required confidence.

It may therefore be safely asserted, that the artificial and natural Alizarine are identically the same; they agree in all their physical and chemical properities, both crystallize in needles, which are usually curved, especially when small, they dissolve in caustic alkalies, forming violet solutions of the same kind; their absorption spectra are identical, their tinctorial powers are the same, the colored lakes which they

form with alumina, iron and copper salts, are of the same tint, and possess the same degree of solubility, and they remain alike unaltered by the action of the light, so that when they are fixed in the cotton fibre, they yield equally fast colors.

Artificial Alizarine has been objected to as a substitute for Madder, on the ground that pure Alizarine alone will not produce the Madder color, other coloring matter being required. But Schunck, who surely is one of the best authorities, has, by a long course of experiments, been led to the conclusion that the final result of dyeing Madder is simply the combination of Alizarine with the various mordants employed, and he recommends extraction from Madder prints as the easiest method of preparing pure Alizarine on a small scale. Perkin could also find nothing but Alizarine on finished Madder print, Purpurine, the merest trace of which could readily be detected by the spectroscope, being entirely absent.

I have already mentioned that artificial Alizarine, as supplied at the present time, is not absolutely pure, but it surely will not be long before a really pure article will be manufactured and sold; meanwhile we may be satisfied with the assurance that the impurities will not interfere with the color produced. The principal organic impurity is Schunck's Anthraflavic acid, which does not combine with the mordants and consequently cannot be injurious.

The result with Madder and its preparations is totally different, because the nature of the impurities is such as to seriously interfere with the brightness of the colors, and it is important to point out this distinction in comparing the value of the two preparations.

All Madder root contains pectin, which is always carried over into all the extracts and preparations; now pectin by itself is probably an indifferent substance, but in consequence of the ease and rapidity with which it passes into pectic acid, it may act very prejudicially in dyeing by combining with the mordants and preventing them from taking up the coloring matters.

Another impurity in Madder is the extractive matter, which by the action of oxygen readily becomes brown, especially at

high temperatures, and contributes, together with the colored resinous matter, to deteriorate the color and to dirty the white ground of the cloth. This is the cause of the uniform dirty, reddish brown tint on a piece of cloth, both on the printed and unprinted portions, the removal of which tint is one of the objects of subsequent soaping.

There cannot be any doubt, therefore, that *Artificial Alizarine is superior and preferable to the natural* from Madder preparations.

It is a compound of known, definite composition and properties. It can be produced chemically pure, and if this has hitherto not been done, the impurities are of such a nature as not to interfere with the coloring effects produced; besides in its present state it is already considerably purer than the best Madder-extract.

Practical tests in the hands of the most competent men have pronounced in its favor. On the other hand, pure Alizarine from Madder is not known as a marketable article.

The extracts, and more so Madder itself and Garance, contain several coloring matters together with a number of organic and inorganic impurities in variable and unknown proportions, which involve a degree of uncertainity in the application, often resulting in loss and disappointment; these impurities always impair the desired effect and involve labor and trouble in counteracting the injury they have produced. And here the greatest advantage of artificial Alizarine will at once become apparent to the printer. Most of the Madder preparations cannot be applied by direct printing, the goods must be first mordanted and then passed through the dyebeck, while artificial Alizarine is mixed with the mordant and printed in one operation; in fact the dyehouse will become useless and the saving in time and labor will be most important.

The time will and must come when the artificial Alizarine will not only gain the mastery over the natural material, but will drive it out of the field altogether. This end will not be obtained in a day, because it is very natural that a new article of commerce should be looked upon with doubt and suspicion in some quarters, especially when it threatens to stifle a most

important industry, and such the cultivation of Madder and the manufacture of its various preparations undoubtedly is.

Great and powerful interests are involved in the Madder industry, and as its very life and existence is threatened, no effort will be spared to kill the new intruder, before it has time to grow strong on its own superiority. But such attempts will be made in vain, because the tendency of our age is to fairly consider any improvement on its own merits; and as soon as the question has been fully and convincingly decided by the printers and dyers, and they find that artificial Alizarine is in every respect at least equal, if not superior to the natural, then the Madder plant will die out, the thousands of acres of land now occupied in its cultivation will be thrown open, and those countries which may at present appear to suffer most by the introduction of the new discovery, will reap the greatest benefit in an agricultural point of view.

It is one of the greatest advantages of modern chemistry to add continually to the wealth of the community and in no other case will this be more strikingly illustrated than here.

The quantity of Madder consumed is immense and so is the money value paid for it. It has been calculated that every year more than 100 millions of pounds are produced, a considerable part of which, one-fifth or perhaps even one-fourth finds its way to this country; taking it at 10 cts. per pound it represents a capital of over $10,000,000, of which at least $2,000,000 are sent from here to Europe, and it may well be asked, whether this sum may not be added to the national wealth by assisting in manufacturing an article from a home product.

Alizarine is at present manufactured in Germany and England only, and although there is no valid reason why it should not be made in this country, it may yet take a long time before this is done. However the starting point of the manufacture is a residue, hitherto useless and valueless, but now commanding good prices; there are no statistical records of the gas manufacture of this country, but it is quite certain there ought to be no difficulty in producing a thousand tons of Anthracene, the value of which would more than cover the

sum which goes every year to Europe for Madder, and which I believe will soon go there for artificial Alizarine.

It is interesting to follow the strange ways certain industries sometimes take. There are so many accidental but vital questions connected with the development of every manufacture that we often see a country fail in supplying itself sufficiently with a manufactured article, although the raw material is abundant, and we find the last exported to a foreign country, there to be changed into the resulting product, which is then returned to the mother country.

Such is the case with the manufacture of all coal-tar colors. England produces immense quantities of Benzol, the greatest part of which goes to Germany, there to be converted into Aniline dyes, a considerable quantity of which goes back again to England. Germany is comparatively poor in the products from coal-tar, and she must therefore go into the English market for the raw material. No other country is so far advanced in the manufacture of the coal-tar colors as Germany, a consequence, no doubt, of the admirable system of scientific and technical education, which produces so great a number of men trained in science and practice. The German manufacturer is thus enabled to counteract the natural disadvantage, he has to contend with.

And the same case holds good with artificial Alizarine, the production of which has hitherto been limited to Germany and England; France, the native soil of Madder, has not yet commenced to manufacture the substitute. The quantity of Alizarine manufactured by the German makers far surpasses the English production, but the principal supply of Anthracene comes from England, which, with its large and densely populated towns, produces the coal-tar under more favorable conditions and in larger quantities, than Germany, where the principal towns are spread far apart.

If Anthracene could be converted into Alizarine without the formation of other products of decomposition, involving considerable loss of Anthracene, the relative proportion as calculated from their chemical composition would be about as

3 to 5, viz. 3 parts of Anthracene should yield 5 parts of Alizarine.

The quantity of coal which must be converted into gas in order to supply the Anthracene for a given quantity of Alizarine may be calculated as follows:

100 tons of Coal yield		3 tons of Pitch,	
100 "	Pitch yield	2 "	Anthracene,
100 "	Anthracene should yield	166 "	Alizarine.

or theoretically 1000 tons of Coal (producing about 10,000,000 cubic feet of gas) should give one ton of Alizarine. It is not known how far the practical result falls short of this calculation, but the quantity of coal required may safely be doubled.

In conclusion I will add a few recipes for printing with artificial Alizarine, which will be found useful in practice.

Recipes for Printing Artificial Alizarine.

Reds.

5 lbs.	Alizarine paste	10 per cent.
16 lbs.	Thickening	
1 lb.	Acetate of Alumina	10 Bé=15°Tw.
½ lb.	Acetate of Lime	16 Bé=25°Tw.

Pinks.

The same, diluted with 2 or 3 parts of Thickening.

For double printing, when deep red is printed on first, the goods must be steamed one hour, before the second printing takes place. After the second printing the goods must again be steamed one hour and hung up to air for 24 hours; they are then passed through one of the following baths at a temperature of 120° to 140°F., remaining in the bath not longer than 1 to 1½ minute.

250 gallons	Water,
60 lbs.	Chalk,
3 lbs.	Tin Crystals.

Or

250 gallons	Water,
40 lbs.	Chalk,
10 lbs.	Arseniate of Soda.

The goods are then washed and brightened as follows: take for 10 pieces of 50 yards each:

1st Soaping	at 120°F.	3 lbs. of Soap,	¼ lb. Tin Crystals.
2d "	at 160°F.	3 lbs. of Soap.	
3d "	at 175°F.	3 lbs. of Soap.	

Wash between each soaping.

Red for Mosaics (Mille-Fleurs).

8 lbs.	Alizarine paste 10 per cent.	
10 quarts	Thickening,	
9½ ounces	Nitrate of Alumina	15°Bé=23°Tw.
19 ounces	Acetate of Alumina	10°Bé=15°Tw.
13 ounces	Acetate of Lime	16°Bé=25°Tw.

Very Deep Red.

10 lbs	Alizarine paste 10 per cent.	
10 quarts	Thickening,	
13 ounces	Nitrate of Alumina	15°Bé=23°Tw.
19 ounces	Acetate of Alumina	10°Bé=15°Tw.
16 ounces	Acetate or Lime	16°Bé=25°Tw.

Another Red without Oil.

8½ lbs. Alizarine paste 10 per eent.
9½ lbs. Acetic Acid 8°Bé=12°Tw.
3½ lbs. Flour.
5 pts. Water.

Boil well and stir till cold, then add.

1st	Acetate of Lime	18°Bé=29°Tw.
2d	Nitrate of Alumina,	15°Bé=23°Tw.
3d	Hyposulphite of Lime,	9 °Bé=13°Tw.

Purple.

3 lbs.	Alizarine paste 10 per cent.	
10 quarts	Purple Thickening.	
6 ounces	Pyrolignite of Iron	12°Bé=18°Tw.
12 ounces	Acetate of Lime	16°Bé=25°Tw.

The printed goods are steamed for an hour or two and then hung up to air for 24 to 36 hours, they are then passed in a padding machine through the chalk and arseniate of soda bath, same as for reds, after which they are washed and soaped in a single soap bath without any crystals of Tin, and if required cleaned with a little bleaching powder.

THICKENING FOR REDS.

12 pounds Wheat Starch,
40 quarts of Water,
4 quarts Acetic Acid 6°Bé=9°Tw.
1¼ pounds Gum Tragacanth,
3 pounds Olive Oil.

Boil the whole well together, and stir till cold.

THICKENING FOR PURPLE.

10 pounds Starch,
27 quarts Water,
3 quarts Acetic Acid,
1⅛ pounds Gum Tragacanth,
2 pounds Olive Oil.

Boil the whole well together, and stir till cold.

The mordants used for the above recipes, are prepared in the following manner, viz.:

ACETATE OF ALUMINA.

30 pounds Hydrate of Alumina are stirred into 6 quarts Acetic Acid, warmed, filtered and the solution reduced to the required degree.

The Hydrate of Alumina is prepared by dissolving

72 pounds Alum in 100 gallons Water,
62 pounds Soda in 100 gallons Water,

and mixing the two solutions; the precipitate thus obtained is well washed, thrown on a filter and squeezed out and dissolved in the acid before it gets dry.

NITRATE OF ALUMINA.

2 pounds Nitrate of Lead.
2 pounds Alum.
2 quarts Water.

Dissolve and separate the liquid from the precipitate by filtration, and dilute to proper degree.

The red is more yellow with Nitrate, than with Acetate of Alumina, and when the first is used more Acetate of Lime must be taken in addition.

ACETATE OF LIME.

A solution of Acetate of Lime at 16° Be contains 25 per cent. of Acetate of Lime; generally one-tenth of the weight of Alizarine paste is required, but it is safer with a fresh quantity of Alizarine, to ascertain on a small scale the quantity required.