Radio-Active Luminous Paints

Substances That Are Being Found of Value During the War

By Arthur H. J. Keane

SINCE the commencement of the present Great War there has been a rapidly increasing demand for such luminous articles as radium watches, luminous compasses *et hoc genus omne*, more especially for use in the trenches and in the open fields, where other sources of artificial light are not available—and, if they were, their use would be accompanied by serious risks. Already since the beginning of the seventeenth century certain substances have been known, such as phosphorus for instance (which possesses the power of shining in the dark), provided they have first been exposed to daylight, gaslight or any other luminous source. The best known of these products is Balmain's Luminous Paint, consisting of a sulfurous combination of calcium made with the aid of a high degree of heat. As at the present time, it was also once used frequently for painting the curbstones at dangerous curves, and in dark positions, so as to render them visible at night. This practice was revived this winter in London where, in the darkened streets, they often proved of very great service. The luminosity of such substances may be explained as follows: Phosphorescence takes place if the sulfide of an alkaline earth (calcium, strontium or barium), or of zinc, be roasted with traces of certain metals and with a fusible addition, mostly in the form of a colorless salt. As foreign metal, copper, zinc or bismuth is more especially used, an extremely small proportion of which is added to every ounce of sulfide. Under the influence of light these substances throw off electrons, or negatively charged ultra atomic particles, while the molecules charged with positive electricity remain behind and form positive ions. As soon as the exposure to light ceases the electrons, owing to the electric forces, endeavor to reincorporate themselves with the ions. Due to the low electric conductivity of the sulfides this, however, only takes place with excessive slowness, and the radiation of light is thus produced by the reunion of the electrons with the ions.

Such phosphorescent substances, however, are not suitable for use in the field, as they always require a prior exposure to light which, in the case of a watch that is always carried in the pocket, can easily be forgotten. A further drawback lies in the fact that, after a few hours, the phosphorescent light becomes so dim or exhausted that it no longer exerts any useful effect upon the eye. This is especially the case with those phosphoruses which give a very strong light immediately after exposure, such as sidot blend (crystallized zinc sulfide).

In the year 1899 Becquerel found that radio-active preparations diffuse a weak light. Furthermore, he found that radio-active substances were also able to impart light-giving properties to other bodies. Thus, for instance, a diamond, when placed close to them, gives off a white light; this is also a process for differentiating between genuine stones and imitations. The luminosity of these substances is caused by invisible rays which emanate from the radio-active substances. The term radio-active is one which is applied to bodies which, in contradistinction to the chemical elements hitherto known, do not exist permanently but in course of time change into other basic substances. Their decomposition is mostly, but not always, accompanied by the irradiation of rays of light. These rays consist mostly of positively charged helium atoms (so-called alpha particles), which are thrown off with a velocity of about ten thousand miles per second, and they compose about 90 per cent of the total radiation. Other substances, on the contrary, send out beta rays, negative or electrons. In spite of their great velocity, which is almost equal to that of light, yet their energy amounts to about 5 per cent of the total radiation. About the same is the action of the last rays, the gamma rays, which—in contradistinction to the two preceding groups—do not consist of single particles but are very short ether waves like the Roentgen rays.

Now the alpha rays are those which have an effect upon certain substances similar to that of light, *i.e.*, they split up the molecules into ions and electrons, the reunion of which is accompanied by the irradiation of light. In order to obtain a good effect it is advisable, especially in these cases, to add sidot blend to the radio-active substance because, as we have already seen, this blend has the strongest effect in producing the radiation of light. That this light soon dies away is, here, not taken into consideration as the sidot blend owing to the continued radiation of alpha rays is, so to speak, permanently re-excited by the admixture of the radio-active substance.

A radio-active luminous paint differs, therefore, from the formerly known phosphorescent substance¹ in the fact that it does not require any prior exposure to light. On the contrary the excitement or action is, in this case, produced permanently by the rays which are thrown off without interruption by the radio-active substance contained in the luminous paint.

As already remarked a radio-active substance is not permanent, but gradually changes into other, also radio-active, stuffs. Thus, for instance, radium changes into a gaseous body (the so-called radium-emanation) which in its turn, changes successively into further solid bodies of which so far six are known to science as Radium A, Radium B, etc., up to Radium F, such a group being termed a "Radio-Active Family." A second and third family are formed by thorium and actinium respectively with their products of decomposition. Due to this gradual conversion the primary, or fundamental, substance is of course not permanently maintained. The periods of time, within which such a substance disappears, differ very considerably. Hence the semi-value periods (*i.e.*, the time within which one-half of the substance has decomposed or "disappeared") are 1,690 years for radium, and about four days only for the radium-emanation. Mesothorium, which is also used for clinical purposes, is obtained from the manufacture of incandescent mantles and has a semi-value period of about five and one-half years; the radio-thorium obtained from mesothorium, and the thorium X obtained from the latter, have a semi-value period of two years and a little less than four days respectively. The same periods for the actinium series are so small, that for practical purposes, it is not necessary to take them into consideration at all.

Of the substances named radium alone possesses a sufficiently high semi-value period so that, apparently, radio-active luminous paints can only be secured by adding radium to the sidot blend. This assumption would be quite correct if the duration of a luminous paint depended merely upon the addition of the radio-active ingredient, and if the sidot blend remained unchanged. As a matter of fact, however, this is also changed in course of time by the continued "bombardment" of the alpha rays, so that the radiation of light steadily declines; this it does all the more rapidly the more powerful the excitation and the brighter the initial light. In very strong luminous paints a marked diminution in the power of the light is noted already after a lapse of six months. Hence it is of no use, at least in the case of a strong luminous paint, to add radium to the ingredients; in fact it is far preferable to use mesothorium which does not throw off any alpha particles itself and, thus, apparently seems to contradict the statements already made. Yet, in truth, pure mesothorium does not produce any light effect. Now technical mesothorium contains from 15 to 25 per cent radium; furthermore it also gradually becomes converted into radiothorium which gives off the alpha rays and is thus highly effective. Hence a freshly prepared mesothorium luminous paint will triple or even quadruple its lighting power during the first four and one-half years, after which it first gradually begins to decline. Hence it is advisable to add a certain quantity of radiothorium to the mesothorium, whereby the throwing off of rays will steadily increase during the first five years, and will not regain its initial value till after ten years; after this latter period it will gradually decrease in power. But if it be taken into consideration that the action of the sulfide of zinc causes a gradual decrease in the lighting effect, then the initial rise in the efficiency of the radio-active substance will tend to counteract the decrease in the radiation of light, owing to the exhaustion of the sulfide of zinc, so that such a mesothorium luminous paint will possess a constant brilliancy during the first three to five years. Also for a further five to ten years they would also give a fairly good light in most cases, so that the useful life of such a luminous paint may be estimated at a period of ten years on the average. In the case of a pure radium luminous paint the lighting power begins to decline *ab initio* due to the exhaustion of the sulfide of zinc, which acts as the light carrier, so that it would become useless within this period.

For very strong luminous paints, however, the addition of mesothorium is not economical. In these cases the exhaustion of the sulfide of zinc is so strong, that the light intensity already becomes practically useless within from one to two years. This could be improved by the addition of pure radiothorium.

¹Not all phosphorescent substances respond to alpha ray.

As the radio-active luminous paints contain about 1-60 milligrams of radio-active substance to every 100 grams of sulfide of zinc, and as a milligram of radium costs from £20 to £25 and a milligram of mesothorium about £10 (radio-thorium is cheaper), hence a really good luminous paint must not be expected to be cheap. This, naturally, gives rise to the temptation to mix cheaper substances into the paints, the principal substitute being thorium X; as its action, however, diminishes by 50 per cent in 3.65 days, the admixture of this substance makes itself apparent within a very short space of time. To determine the exact amounts of radium, mesothorium and radiothorium contained in a luminous paint is a difficult matter for the expert, and quite impossible for the dealer and buyer. To render such an investigation possible quantities of about 15 grams would be necessary; furthermore, as the radio-active substances are added in the form of insoluble salts, it would be necessary to chemically flux the luminous paint. These are processes which can only be carried out with a very well equipped laboratory while, owing to the large quantities of the various substances required, they are very costly. The purchase of a radio-active luminous paint is, therefore, more or less a question of blind trust and should only be made from some highly reputable firm or factory whose reputation is in itself a guarantee for the goodness of the paint.

It is also extremely easy to make a mistake even when merely testing the substance externally. As sidot blends belong to the so-called phosphorescent substances, and become luminous after exposure to light, hence a radio-active luminous paint which has been exposed to day or lamplight appears much more luminous than when it has lain in the dark for some time. It must, therefore, first of all be placed for several hours in a dark room or in a closed receptacle before it is possible to test its actual lighting power. A simpler way is to expose the luminous paint for a few seconds to dark-red light—such a lamp as photographers use in a dark chamber for instance—as the red (and more especially the ultra-red) rays will cause the phosphorescence to disappear very rapidly.

Luminous paints are mostly used in a powdered form, and are applied to the articles it is desired to coat with the aid of an alkaline gum-lac (acid lacs would destroy the sulfide of zinc). This process, however, is not a practical one, as the lac can easily entirely envelop the individual grains or particles, and thus hold back and prevent the alpha particles thrown off by the radio-active substance from exerting their influence.

A coating of lac is nevertheless necessary so as to retain the gaseous emanations which, otherwise, would escape into the surrounding air; it is precisely these emanations and their products of decomposition, as they also mostly throw off alpha rays, which substantially enhance the luminous effect.

Radio-active luminous compounds are being more and more widely used—especially since the outbreak of the present War of the Worlds. For watches relatively weak paints suffice, but for compasses a much stronger compound must be used because, in the twilight prevailing in the open, the eye is always adapted to the reception of a weak light effect. Especially strong compounds must be used when it is desired to distinguish not only individual points, but also figures or letters, at a considerable distance. These paints are also largely used just now in connection with military work but, for obvious reasons, it is not possible to deal with these at the present juncture. We may, however, mention that very great benefit has been obtained from these paints when used at night time in the streets, darkened to prevent attacks by the German Babykillers. Luminous buttons for pedestrians, walking sticks and umbrellas with luminous handles, luminous buckles and shields for mens' hats and policemen's helmets, have all done good service and prevented many a collision on the pavements and loss of life when crossing the roads. In dark private roads, letter boxes, trees, and so on, have also been given a few dabs of this shining mass, to the great gratitude and relief of those whose business or pleasure compelled to wander late at night through the Stygian darkness of the London streets in War Time.

EDITORIAL NOTE.—Commenting on the above article, Dr. Charles H. Viol, Director of the Radium Research Laboratory, Pittsburgh, has the following to say: "As far as I know mesothorium has only been produced on a commercial scale in Germany, and while some amounts of this material are being used at present, even in this country, in the production of luminous compounds, I

am at a loss to understand where any considerable supplies of this material might be obtained.

"You can realize the difficulties of the mesothorium producer when you know that there is one part of radium for every three million parts of uranium in an ore, whereas because of the shorter life of mesothorium, there is only one part of mesothorium (measured in terms of the gamma ray radium standard) for something like sixteen million parts of thorium. Consequently the mesothorium producer has to produce a rarer product,

and has to market his material at a lower price than radium; and this, with the present high cost of production, does not conduce to mesothorium production.

"Another point with regard to the use of radium in phosphorescent materials, which is the subject of error, is that the addition of radium to any phosphorescent material will produce a permanent luminous compound by reason of the action of the radium rays. This is not the case at all, since only those substances which are

sensitive to the alpha rays, as is the case with zinc sulfide, can be used for this purpose. Willemite, which glows splendidly under the beta and gamma rays of radium, shows no alpha ray scintillation, and consequently only a very low degree of luminosity when mixed with radium. Calcium sulfide shows no luminosity due to alpha rays when mixed with radium. Alone, as a phosphorescent substance it is superior to zinc sulfide in its power of maintaining phosphorescence for a number of hours."

The Oil Fields of the Apsheron Peninsula*

Richest Lands in the World Contained Within Russia's Barren Promontory

AMERICANS, who now so often "strike oil" without having anything to do with petroleum, can hardly be expected to know that the most remarkable oil land in the world is not in Pennsylvania, or even in the United States at all, but is mainly included in the famous Apsheron Peninsula, which projects from the southern border of European Russia into the western side of the Caspian Sea.

The peninsula, with perhaps a part of the Caspian Sea area, is in fact the center of the most prolific and complicated oil-bearing axis in the world. It is a part of the tectonic (or earth-building) axis which extends to the west and northwest through the Caucasus range, the Balkan ranges, and the Carpathians. This axis is oil-bearing in Galicia and Rumania. In the Balkans there are no known oil deposits. But on the north slopes of the Caucasus very rich fields have been tapped, as at Grozny and Maikop; in the Apsheron Peninsula we reach the richest oil lands yet discovered. Apparently the oil-bearing sands of this axis extend even farther to the east and northeast, for there are the newly developed Emba fields just to the northeast of the Caspian, and other sources, as yet little exploited, in the trans-Caspian districts.

Though Russia has had to yield first place in total oil production to the United States, experts hold that the ultimate resources of the fields about the Caspian are likely to prove greater than those of any other regions yet known. Even before the recent exploration of the Emba and other fields in the Ural Province, it was estimated that the Russian oil fields covered an area of at least 14,000 square miles. How little this has been touched will appear from the fact that previous to 1903 the whole of Russian petroleum had been taken from an area of less than 20 square miles, while all but a small fraction of the total quantity had come from less than 10 square miles of land. Every year discloses new areas where signs of oil and gas promise large yields in the future.

FROM FIRE-WORSHIPPERS TO PIPE-LINES

The history of petroleum on the Apsheron Peninsula is a long and varied one. The natural gas exudations and oil deposits of this region have been known for many centuries back. The existing site of the Temple of Fire-Worshippers at Surakhany, near the point of the peninsula, has been visited by members of that cult for more than 2,500 years. Baku petroleum, according to historians, has for centuries past been collected by the Persians and sent into Persia and inner India, where the white variety that is found in several parts of the peninsula was used as a medicine both internally and externally.

Formerly the Apsheron Peninsula belonged to Persia. Peter the Great annexed Baku in 1723; it was restored to Persia in 1735, and again reoccupied by Russia in 1806. The Government granted a monopoly of the first infant petroleum industry here. Later, in 1872, the monopoly was abolished and an excise tax on the industry substituted. In 1877 this tax was removed, and then the industry began to expand rapidly. This was six years after the first oil well was bored on the Balakhany plateau. Previous to 1871 all Russian petroleum was obtained from hand-dug surface pits, of which the deepest was seldom more than fifty feet. With the boring of wells came gushers, and such a sudden increase in the supply of petroleum that for a time the industry was quite demoralized by the superabundance. It was the famous Swedish brothers Nobel, Ludwig and Robert, who actually revolutionized the Baku oil industry. They built and operated at Baku a modern refinery, run on the most scientific methods, and built the first pipe-line from the Balakhany field to the refineries at "Black-town" (Chorny Gorod), which is the oil-industrial part of Baku, to the eastward of the residence and business district. Before this, the oil from Balakhany had been

conveyed to the refineries in barrels on two-wheeled Tartar carts, a long string of these occupying the "road" all day long. Other firms, at first as skeptical about the pipe-line as the carters were enraged, were soon converted, and the oil carts were wholly abolished. Tank vessels plying on the Caspian to the mouth of the Volga soon followed, and the modern industry was established.

NATURE OF THE APSHERON COUNTRY

The peninsula itself offers a striking topography and appearance. As its base, or western part, nearest the Caucasus, it reaches an elevation of about 900 feet, declining towards the Caspian until along the shore its greatest height is about 100 feet. It is bare and waterless except for salt lakes,—altogether austere and forbidding in appearance.

No study for the geology of the region has been made by the Russian Government, and what is definitely known of it is contained in the records of engineers and of companies which have done much exploitation work. Both in the peninsula and farther west, the oil-bearing strata antedate the formation of the ridges of the Caucasus, which are of comparatively recent formation.

THE DEVELOPED OIL AREAS

The chief oil areas so far developed on the peninsula are the three older fields,—Balakhany, Saboontchy, and Romany, which embrace an area of about four square miles on a plateau at an elevation of about 175 feet above the Caspian; the Bibi-Eibat, three miles south of Baku; and the new fields of Binagady and Surakhany. The first drilled oil well in Russia was put down in the Balakhany field, where previously, as elsewhere in Russia, oil had been obtained only from hand-dug wells or pits. Drilled wells followed in the other two of the older fields, and in a short time this small area had proved itself the richest patch of oil land in the world.

Bibi-Eibat is a peculiar region,—a low-lying, curved bay of flat land on the Caspian shore, hemmed in by bluffs. Here the oil-bearing series of strata, which are estimated at 2,000 feet in thickness, dip under the Caspian Sea. In order to get at the oil in this very rich field, the Russian Government some years ago began to fill in along the sea edge, so as to make the deeper-seated oil accessible to boring. The results have amply justified this measure in a very large oil production. The oil at Bibi-Eibat differs from the other oils by its richness in paraffin.

OIL GEOLOGICAL CONDITIONS

The first geological condition necessary to the storage of petroleum is a porous stratum in which the oil can accumulate; the second essential is the presence of an impervious stratum overlying the oil bed to prevent the displacement of the oil by water, and to stop the escape of petroleum gas. The pressure of the confined gas on the stored oil is of great practical importance, since it is the gas pressure which produces "gushers," or fountains, from which the most rapid output of oil is obtained. The first condition is inevitable if the formation of the petroleum is the result of the decomposition of organic matter contained in the stratum, for the oil simply takes the place of the original substance. But the commercial value of an oil district depends upon the degree of porosity of the oil-bearing strata, as the degree of porousness determines how large an oil area can be drained by a single bore-hole in a definite time—in other words, the porousness determines the rate of production. The second condition, that of the overlying, impervious stratum, is probably responsible for the existence of the petroleum, since without this covering oil would probably never have been formed, or, if formed it would have escaped. It is the amazing porosity of some of the Baku oil sands, says A. B. Thompson, a British expert on the Baku district, that has led to such phenomenal producers in these fields; 200, 300, and 400 cubic feet of petroleum, mixed with nearly an equivalent weight of sand, and hundreds of cubic feet of gas being ejected per minute from a bore-hole.

The oil of the Apsheron Peninsula is secreted in lens-shaped pockets of sand which do not communicate freely, if at all, with each other, although occasionally, after the removal of much sand and oil, as may be caused by the perforation of strata by a bore-hole, the barriers which have separated distinct oil beds may be broken down, and communication between them established. There is no relation between the sea-level and the levels of oil in wells, for both on the Balakhany plateau, and at Bibi-Eibat at sea-level, the petroleum at times spouts up two or three hundred feet above the Caspian level; while at other times the oil level is as much as a thousand feet below the Caspian surface.

The pressures met with in the Russian fields are asserted to be almost beyond question due to the presence of gas held in solution in a very compressed state by the petroleum, until release of pressure is given by a bore-hole penetrating to the gas-charged oil.

Mr. A. B. Thompson has written so much the best account of the Baku and Apsheron oil fields, both in their scientific and picturesque aspects, that no apology is needed for giving here some brief quotations from his book "The Oil Fields of Russia."

WHEN OIL "FOUNTAINS" SPOUT

"Excitement" is a term used by Thompson for the striking phenomena which attend the flowing of an oil "fountain," or "gusher," as an American would call it. He says of this:

When, in the Baku district, a fountain is flowing, the disturbance created in the oil stratum must be terrific, for the surface of the ground quivers for a radius of a quarter of a mile, and the noise produced by the violently expelled oil, gas, and sand can be heard for miles. It may be impossible accurately to describe the subterranean movement at such moments, but a little consideration will inevitably lead one to construct a mental picture of the kind of active changes taking place a thousand or more feet below the surface.

It is not improbable that the larger fountains in the Baku oil fields are partly due to the excitement or reaction occasioned by a flow of oil. At first, oil steadily overflows the casing, through supersaturation with gas; but immediately the heavy column of liquid is partly expelled, and a large part of the resistance removed, a violent rush of gas, carrying with it oil and sand, occurs toward the shoe of the tubes, with the result that exit is suddenly closed, and a violent check is momentarily imparted to the moving mass in the earth. For an instant the slow movement of a solid plug in the tubes prevents further admission to the tube; but as the upper pressure is still more relieved, and the pressure of gas below rises, the temporary resistance of the sand-plug is overcome, and the mass is ejected with terrific impetuosity up the tube. The sudden release of pressure thus afforded causes another inrush of sand, and the action just described is repeated. There is, in fact, a constant water-hammer action going on in the sand stratum, which probably plays no small part in opening up oil ground for a considerable area around the bore-hole—an area that would, but for this "excitement," remain unaffected.

NATURAL PURIFIED OILS

The Surakhany gas sands have for centuries been known to furnish a little highly refined volatile petroleum, of a straw color, denominated "white oil," which commanded a ready sale at one time for medicinal purposes and branches in the early arts. The Surakhany product has a specific gravity of 0.780, and its composition is—

Benzine.....	48.9 per cent
Kerosene.....	43.9 per cent
Other oils.....	7.2 per cent

Its highly volatile character, which causes a sensation of cold and pain when applied to the skin, has very likely led to its supposed curative powers, but in any case the extent of its use must have been strictly limited, as the quantity procurable is very small.

*From Russia for April, 1917. Copyright 1917 by R. Martens & Co. Inc.