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ICHTHYC OIL'

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In the vicinity of Seefeld,² in the Austrian Tyrol at an altitude of 1,000 meters lies a rock formation known geologically as Seefeld shale. It is found in veins varying in thickness from 20 cm. to 100 cm. Enveloping this shale is the Gallenstein formation containing many fossil gastropods. The occurrence of this particular mollusk in large quantities dates the formation as Silurian.

The Seefeld formation is a specific bituminous shale which yields a crude oil from which Ichthyol is made. Centuries ago, the Tyrolian peasants would collect this shale, boil it with water in large pots, and skim off the black tar which came to the top. To this tar was attributed miraculous healing power, and as a curative agent it gained wide fame and usage throughout adjoining districts.

¹Ichthyic Oil is the name adopted by The National Ichthyic Oil and By-Products Interests now developing the only known Ichthyol ore deposit in the United States. Actually, the word Ichthyol should be used only to designate the Austrian product, as it is a registered trade name. However, to simplify the terminology, Ichthyol will be used indiscriminately throughout this article to designate both products.

This paper does not attempt to confine itself to original research, but hopes to convey some of the interesting information concerning this pharmaceutical.

The writer was retained in the summer of 1935 to study the extraction and refining process of the local deposit and to test the finished product.

²Dinkelspiel, *The Merck Report*, Vol. 44, No. 1, p. 7.

Ichthyol emerged from fable and local seclusion in the age when so many prodigious contributions were first introduced to mankind, the last two decades of the nineteenth century. But no sooner was this substance stripped of its legendary encumbrances than science and pseudo-science submerged it in such an avalanche of attributes that it has yet to shake off some of the claims based more on enthusiasm than facts.

In 1883 Unna introduced Ichthyol to the medical profession as a new medicament for treating certain skin diseases. The therapeutic value was not recognized immediately, but ultimately its fame was carried on the wings of the wind, the unquented being recommended for practically every conceivable human ailment. Today the properties of Ichthyol judged on a purely scientific basis make it one of the blessings of mankind, since for certain specific uses it has no superior.

The substance introduced by Unna was not the black, tarry material used by the Tyrolian peasants for over five centuries, although it looked and smelled similar. The Thierschen oil of legend was subjected to destructive distillation in iron retorts, and the distillate sulfonated with concentrated sulfuric acid, producing a black, tarry, corrosive mass—ichthyol sulfonic acid. This acid was neutralized with ammonium carbonate and the resulting salt called, for the lack of a better name, ammonium ichthyol sulfonate. This substance, an organic salt, was called Ichthyol (*Ichthyc*—Gr. for fish and *Oleum*—L. for oil), a name that implies that the substance is a fish oil. However, it is not an oil in any sense.

One mile from the court-house at Burnet, Burnet County, on the property of J. T. Clements and adjacent lands, lies the bituminous rock from which Ichthyol is made. The bitumen still intact in the fossiliferous strata in which it was originally deposited, occurs in two known strata—friable and porous. In a large part of the formation the rock seems to be composed entirely of fossils, but on closer examination one sees about 20 per cent of binder present. The fossils are mainly elongated Silurian gastropods. The fossil beds vary in thickness from two to six feet. The upper stratum, from

three to six feet thick, is exposed in many places; the lower stratum, two to four feet thick, lies four to six feet below the upper bed. Separating the fossil beds is a grey, soft stratum of weathered shale, which has been given only a casual examination. This rock containing scattered fossils, disintegrates, when exposed to the weather for several months, into a powder containing about 10 per cent of hard particles varying in size from one-quarter of an inch to several inches. The approximate composition of the decomposed material is 30 per cent sand, 70 per cent clay, mixed with calcium carbonate, and a small amount of bituminous material.

The ore-bearing strata contain as high as 15 per cent of the bitumen. The material left in the residue after extraction of the bitumen contains about 40 per cent sand, the remainder being chiefly calcium carbonate. Analyses of the basic rock material were only approximated. Further work will be required to determine the exact composition of the stratum.

James M. McClave³ of the Western Research Corporation states,

My estimate is based on outcrops and open cuts I made when I examined the property, showing a well defined stratum of oil bearing rock ranging from 3 to 6 feet in thickness, and, with an average of 3 feet, will produce 6,700 tons per acre. One ton of oil bearing lime rock will produce 80 pounds of crude ichthyol, or 536,000 pounds per acre.

About three years ago I received a sample of the crude material taken from a stratum about 5 feet below the one I examined. The test on this sample for oil content was practically the same as my samples from the upper stratum. Where the sample was taken from the lower stratum it was 4 feet thick, and, taking an average of 2 feet in thickness, would add 4,300 tons per acre to my estimate, or a total of 11,000 tons per acre.

McClave's report was based only on the properties controlled by the National Ichthyic Oil and By-Products Interests. The writer has observed the same overlying formation in cuts and creeks nearby, that would add about 300 acres to the now known deposit. There is no doubt concerning the large amount of available material present in Burnet County.

³Report dated June 12, 1933.

The curative properties of this mineral have been known to white man since the first settlers' came to the region. They would collect the "black tar" in the summertime and use it as a salve for cuts, sprains, bruises, insect bites, "rash", rheumatism, and many other ailments. When the extruding supply became insufficient they would dig and sometimes find pools of the dark, tarry fluid. This would be carried away in buckets to be used as a salve, to grease wagons and other farm implements, to treat cattle and stock, and mixed with "coal oil" as a paint.

The exact nature of the substance was discovered in 1913 by a Mr. Stringer, who having lost an arm, had had this "tar" used on the healing wound by a local physician. Mr. Stringer recognized the odor as a familiar one and finally placed it as Ichthyol odor. Samples were sent to several testing laboratories over the United States, but reports were negative. Finally, a sample was sent to Germany for testing and was declared to be Ichthyol ore. Information concerning the chemical and physical nature of Ichthyol and its ore is meager, since to recognize the ore it is necessary to prepare Ichthyol from it. Since in 1913 there were no known American deposits of Ichthyol ore, and the substance was, and still is, manufactured in Germany, it was not surprising that our analysts would not commit themselves concerning the positive identification of this bitumen.

In 1917, when the United States was deprived of European sources of Ichthyol an attempt was made to develop the Texas deposit. The process attempted was the destructive distillation of the ore in large retort made of boiler plate. The retort would not stand the necessary heat, and the process proved too expensive because of the unavoidably frequent renewal of the fire plate of the retort. It seemed impossible also to secure sufficient information concerning the refining of the distilled oil, although the company did produce some Ichthyol.

In 1927 the National Ammonium Ichthyolate Company

⁴The author wishes to express his appreciation to Miss Kate Sorrels, Mrs. L. C. Chamberlain, and Rey Fry for their co-operation in securing much of the early history of the deposit.

was organized to develop the property. The ore was shipped to Austin for refining, but the depression soon terminated the activities of that concern.

The present company, organized in 1931 under the direction of Dr. J. Odd Hamilton, has had several engineers and chemists working on the process and is now in a position to start production.

The main difficulty in the development of this deposit is the lack of reliable information. McClave⁵ states,

After investigating the former methods of handling the crude material and the extraction of the oil, I realized that there were no practical data available for the economic recovery of this high grade oil. . . .

From available data it seems that attempts to produce Ichthyol were made without sufficient research to assure a uniform, marketable product. Operations were attempted before adequate information on all phases of the process was established, and the result was failure.

There has been much controversy concerning this deposit. Some state that there is no Ichthyol present, a true statement which, however, needs an explanation. Ichthyol is not present in either the Texas or the Tyrol deposit. Ichthyol is a water-soluble substance made from the oil obtained from the destructive distillation of a specific type of bitumen. An analyst will not find Ichthyol in a sample of the ore. In view of the fact that there is no specific test for Ichthyol and that only meager data are available concerning its properties, a statement concerning the presence or absence of Ichthyol ore would be useless unless an exhaustive study were made. The unanimous opinion of those having made such a study of the Texas ore deposit is that it will produce ammonium ichthyol sulfonate of equal, if not superior, therapeutic value than that produced from Seefeld shale. The chemical and physical properties are identical.

The oil obtained from the destructive distillation of the ore is dark red in color and contains about 10 per cent organic sulfur. It is thought that the organic sulfur compounds are the active therapeutic agents. If the oil is sulfonated with

⁵Loc. cit.

concentrated sulfuric acid, and neutralized with ammonium hydroxide, a water soluble mixture of organic salt is produced that collectively is called ammonium ichthyol sulfonate.

It is stated⁶ that ammonium ichthyol sulfonate has the formula $C_{28}H_{36}S_2O_6(NH_4)_2$, or $C_{28}H_{36}SO_2(SO_3NH_4)_2$. The ichthyol radical would be $C_{28}H_{36}SO_2$. From the information given, the implication is that ichthyol is a definite chemical compound, although all evidence indicates that it is a mixture. From the destructive distillation of complex organic compounds a mixture of oils is obtained. The distillate obtained from retorting this bitumen does not have a definite boiling point, therefore it is not a pure substance. Its distillation range covers more than 100°C. Any fraction may be sulfonated and ammoniated to give the same type of salt. Since the distillate is sulfonated without further fractionating, and is a mixture of unsaturated organic sulfur compounds, the result is a mixture of ammonium sulfonate compounds. The substance may be called ammonium ichthyol sulfonate, if the collective meaning of the term ichthyol is understood.

Ichthyol is a reddish-brown, syrupy liquid with a definite bituminous odor and taste, completely miscible in water, glycerol, oils and fats in all proportions. When heated it puffs up with some carbonization and volatilizes on continuous heating. It is partially soluble in ethanol, methanol, isopropyl, diethyl ether, chloroform and benzene. The addition of a strong mineral acid causes the formation of ichthyol sulfonic acid in a dark resinous mass, only slightly soluble in water, which may be partially reprecipitated by the addition of a strong mineral acid or an alkali-halide. Iodine, bromine and chlorine each causes Ichthyol to precipitate. Whether the precipitate is an additive compound of Ichthyol and the halide was not determined. The ichthyol sulfonates of the alkali-metals and ammonia are soluble in water. The salts of the alkali-earths, zinc and iron, are insoluble in water. Silver, mercurous and mercuric ichthyol sulfonates, were prepared with some difficulty and were found to be insoluble.

⁶Remington & Wood, *United States Dispensatory*, 12th ed., p. 1433. N.N.R., 1917, See Ichthyol.

Ichthyol contains 46 to 48 per cent water, 5.5 to 6.3 per cent ammonium sulfate, the remainder being ammonium ichthyol sulfonate. The total ammonia should be 3.0 to 3.5 per cent. The ammonium sulfate results from the excess of sulfuric acid used in the sulfonating process on neutralization. Sulfur is present in three forms: the organic, or inherent, sulfur; the sulfonate group introduced by sulfuric acid; and as sulfate in the ammonium sulfate. Organic sulfur is present in the finished product to the extent of approximately 5.5 per cent, the total sulfur content varying between 10.0 and 10.5 per cent. Over one-half of the sulfur appears in the form of organic sulfur that is supposed to give the substance its therapeutic properties.

The efficacious therapeutic properties of Ichthyol are in the field of dermatology for the treating of certain specific skin diseases. Since its introduction by Unna in 1883, science has not produced a superior substance, though many have been introduced. Pure, it is a mild irritant when applied to the skin. When dilute, it is an emollient and is used where stimulating action is desired. It is generally used as a 20 per cent ointment with petroleum jelly or lanolin as a base, or in aqueous solution, although it is often used pure and as a 10 per cent ointment or solution. Ichthyol has slight antiseptic action and can penetrate the skin, as is evidenced by the increased sulfur content of the urine after use. It has been employed with success as a local alternative and anodyne in the treatment of chronic eczema, acne, intertrigo, lupus, and in infections of the subcuticle as cellulitis or furunculosis. It has been recommended for the treatment of erysipelas, tuberculous lymphadenitis, frost bites, sprains, sub-acute and chronic gout, and rheumatism, but its value in treating these diseases is doubtful.

Helmerts⁷, performing a series of experiments on the metabolism of Ichthyol, found that most of it was excreted unabsorbed in the feces. The oral dosage from 1 to 15 minims,⁸ is gradually increased to 10 minims as the stomach becomes tolerant.

⁷Helmerts, V.A.P.A., 125, 135 (1894).

⁸15 minims=1 gram.

It would be difficult to find a substance that has been flattered to the extent of Ichthyol in the number of substitutes that are "just as good." Many bituminous deposits will give a substance that looks and smells similar to Ichthyol and undoubtedly have some therapeutic value.

Practically all petroleum contains a small amount of material that will produce Ichthyol-like material, but a critical chemical and therapeutic analysis shows the substitutes to be inferior. If a heavy naptha is refluxed with sulfur for six hours, the excess sulfur filtered out, the filtrate sulfonated and ammoniated, about 10 per cent of a reddish-brown, syrupy liquid with a somewhat bituminous odor is obtained, which has doubtful therapeutic properties and is decidedly poisonous when taken internally.

After fifty-six years in a scientific world, Ichthyol is almost as much a mystery as it was five hundred years ago. We know so little about it that the sum of our knowledge may be termed almost nil. What it is has not been solved; to what it owes its therapeutic value is a guess, and it cannot be produced to meet rigid chemical standards. Much research is yet necessary before Ichthyol can be solved. But mankind is to be ever grateful to those myriads of tiny mollusca, the gastropods, that inhabited the warm seas when our earth was still young, millions of years before the dinosaurs began their dominance.