EXPERIMENTS WITH RADIOLUMINESCENT DIALS FROM MILITARY IWC WATCHES.

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NTRODUCTION

To be able to read the time in the dark watch manufacturers used radio luminescent paint on the dials and hands. However, the compounds used to achieve"the glow-in-the.dark" have changed with time. Until the midsixties the radioactive element RADIUM-226(RA-226) was used. Radio luminescent paint consisted of RADIUM-226 mixed with Zinc Sulphide powder.

During WW II, German military watches used on ships and submarines, were equipped with a full luminous dial. Controversy exists about the exact composition of the applied luminous material, but the main part is ZINC SULPHIDE, a non radioactive phosphorescent material.

From 1968 onwards, RADIUM-226 has been abandoned and predominantly replaced by TRITIUM (H-3), also mixed with ZINC SULPHIDE crystals.

TRITIUM is the radioactive nuclide of HYDROGEN (H-2). Currently a non radioactive material is used: SUPER LUMINOVA. Among many watch manufacturers, IWC first used radium-226, followed by ZINC SULPHIDE, TRITIUM and SUPER LUMINOVA, respectively.

Probably, the first military IWC watch where Radium-226 had been applied was the service pocket watch of the Corps of Engineers(USA) during WW I. As a sub contractor for ULYSSE NARDIN, IWC manufactured about 2000 pocket watches. The main contractors were VACHERON CONSTATIN, ULYSSE NARDIN and to a lesser extent ZENITH.

They were unable to deliver large quantities of pocket watches within a short time span and therefore they hired sub contractors, among them IWC.



fig.1: IWC K.M. pocket watch with luminous ZINC SULPHIDE dial

The second military watch containing RADIUM-226 was the famous "Grosse Fliegeruhr/Big Pilot", cal.52 S.C. from 1940.From 1942-'44, IWC made for the German Navy the large cal.67 Kriegsmarine/Observation watch(K.M.). According to JÜRGEN KING, head of the IWC museum, about 1500 watches had a white enamel dial and 1000 were equipped with a full luminous dial, containing ZINC SULPHIDE, without the addition of RADIUM.

The third military watch where IWC applied radio luminescent paint was the so called WATCH WRIST WATERPROOF (W.W.W.).



fig.2: IWC W.W.W with RADIUM dial

Often this watch is wrongly named Mark X.

Before sending 6000 W.W.W's for the BRITISH MINISTRY OF DEFENCE (MoD) in 1945, IWC had used RADIUM on the so called MARK IX and other civilian pocket and wrist watches. The naming is also incorrect and the correct name is "Special watch for Pilots". Moreover, it was not a military watch.

In 1948 IWC 's most famous military watch was launched for the Royal Air Force: the MARK 11. The original models produced for the ROYAL AIRFORCE (RAF), had a RADIUM dial and during the sixties the Radium paint was replaced by TRITIUM. A small circle with a T inside printed on the dial indicates the use of TRITIUM. Many watches coming in for service by MoD or later by Schaffhausen had their RADIUM dial replaced by a TRITIUM dial.



fig.3: IWC Mark 11 with TRITIUM dial

After the MARK 11 with its excellent cal. 89 movement, it was some time before IWC produced their next military watch.

Together with ALEXANDER PORSCHE, JÜRGEN KING from IWC developed the TITAN DIVERS OCEAN BUND.

In some of the models (ref. 3314,3509 and 3519) a red circle with 3H was printed on the dial, indicating that TRITIUM had been used.



fig.4: IWC Ocean BUND with TRITIUM dial

RADIUM-226 has an extremely long half-time life of 1600 years. It means that it will last 16 centuries before the radioactive emission has halved. This nuclide produces Alpha, Beta and Gamma rays. Alpha rays have virtually no ability to penetrate the body while Beta rays are capable of penetrating the skin, but they are completely stopped by the watch case back or even by a plastic crystal.

However, Gamma rays produced by RADIUM and its daughter nuclides are potentially dangerous for the human body. They pass for a part a steel shield like a watchcase back and more easily they pass the watch glass. From here, they may penetrate the body and damage the living cells.

The extreme long half-time of RADIUM-226 makes that a watch manufactured in 1945 has lost insignificant radioactivity and behaves "as new".

Yet, 60 year old RADIUM dials do not continue to produce sufficient radio luminescence anymore. This is due to the continuous bombing of ZINC SULPHIDE by RADIUM and its decay products. This process breaks down the structure of Zinc Sulphide crystals. The radio luminescence is not coming from the RADIUM but from the non-radioactive ZINC SULPHIDE molecules. The Alpha, Beta and Gamma rays are capable of disturbing the orbits of electrons surrounding atoms such as ZINC and other elements. When the excitation is over and the electron is caught again by the atom, energy is released as a flash of visible light: photon energy. At the end of World War II, concerns arose about the use of RADIUM-226 in timepieces and instruments. Already 20 years earlier, RADIUM dial painters had died from cancer caused by radiation. PAUL FRAME from Oak Ridge Associated Universities has written an excellent overview on the danger of RADIUM-226. He quotes ROSS MULLNER who said:"There were so many RADIUM painters in Switzerland that it was common to recognize them on the streets even on the darkest nights because of the glow around them: their hair sparkled almost like a halo".

And ROBLEY EVANS stated: "The original practice of using the mouth to put a point on the brush was common. For wiping and tipping the brush the workers found that either a cloth or their fingers were too harsh. The paint so wiped off the brush was swallowed. In fact, the instructors sometimes swallowed some of the paint to demonstrate that this was harmless".

Death due to RADIUM induced cancer, especially in the area of mouth and jaws was observed from 1925 onwards. This experience together with the long half-time of RADIUM-226, the emission of Gamma rays and above all the hazardous radioactive source that is created when multiple watches are kept in one room for service or storage, had led to serious concern.

Many countries have developed guidelines about how to deal with hazards from luminised timepieces in watch/clock repair.

ZINC SULPHIDE has been used as a scintillation detector, because it emits light on excitation with X-rays or electron beams. This is why the combination of RADIUM-226 and Zinc Sulphide produces a continuous glow-in-the-dark effect. However, Zinc Sulphide itself exhibits phosphorescense due to impurities on illumination with blue or ultraviolet light. When traces of copper are present in the Zinc Sulphide crystals, the typical glow-in-the-dark greenish color is produced. This can be seen on X-ray and radar screens, but apparently also on watches.

TRITIUM (H-3) is a low energy Beta emitter. It does not produce Alpha nor Gamma rays. Its half-life is 12.3 years. The advantages of TRITIUM over RADIUM are obvious. Not only its half-life is a fraction of that from RADIUM but the lack of Gamma rays makes it much less dangerous for the human body. Although the Beta rays are completely blocked by the watchcase and the crystal, TRITIUM may leak outside of the watch. TRITIUM, like HYDROGEN, is a gas incorporated in a polymer substance together with luminescent material (usually Zinc Sulphide). As a gas, Tritium might

escape from the dial and leak outside the watch where it can be inhaled or may penetrate intact skin. Theoretically, this may happen to the owner and also to a person nearby. A clear disadvantage of Tritium is that the short half-life will not provide sufficient luminescence for the dial to glow adequately after 10-15 years.

MATERIAL and METHODS As avid IWC collectors (AVDM, HG) and as medical doctors (AVDM, RC), working with X-rays, nuclear medical products and techniques, we have measured the radioactivity produced by IWC military watches. The W.W.W.-watch with RADIUM-226 dial, the K.M.cal.67 pocket watch with full luminous dial, the MARK 11 with TRITIUM dial and the Ocean Bund ref.3314 with TRITIUM dial have been tested.



fig.5: Geiger counter for detection of radioactive contamination

fig.6: Geiger counter to measure radiation exposure rates

We have measured radioactivity using 3 different types of radiation detectors

- Measurements have been performed at distances varying from 0 cm, 10 cm and 50 cm between watches and detector.
- Radioactivity was counted while the dial was directed towards the detector and with the case back towards the detector.
- In addition, we have determined how much Gamma ray activity is passing through the wrist.

As we are not completely sure about the exact composition of the ZINC SULPHIDE containing compound on the K.M.POCKET WATCH, we counted radioactivity quantitatively anyhow. This was done over a period of 18 hours using an extremely sensitive scintillation counter, consisting of a SODIUM IODIDE crystal placed in a lead container. The lead wall from this container is 5,3 cm thick. We expected not to find much radioactivity outside watches equipped with a Tritium dial as the emitted Beta rays are blocked inside the watch.

To express the absorbed radiation dose during a certain period of time we used the unit microSievert/hr. In older publications often MICROREM/hr¹ has been used.



fig.7: Sodium lodide scintillation detector

One microSievert equals 100 MICROREM, one MILLISIEVERT equals 100milliRem. Measurements were performed 3 times. The average result from 3 measurements was taken. Because of the rarity of these watches, only one watch from our own collection could be tested.

¹ The röntgen equivalent in man or rem (symbol rem) is a unit of radiation dose. The conversion factor has been readjusted from 1 to 1.07185 so that 100 rem equal 1 sievert; the sievert is the recommended SI derived unit, and in many cases is the legally prescribed unit.



No radioactivity, exceeding the background radiation could be detected outside the ZINC SULPHIDE dialed K.M. pocket watch. The MARK 11 and the OCEAN BUND, both with TRITIUM dial, did also not emit measurable radiation.

- We found 0,015, 0,013 and 0,013 MICROSIEVERT/HR, respectively.
- The "average" back ground radiation is 0,011 MICROSIEVERT/HOUR.

As expected, the W.W.W.-watch, containing the Radium-226 dial emitted measurable radioactivity.

With the dial towards the detector we found:

- Distance 0 cm: 2.3 MICROSIEVERT/HR.
- Distance 10 cm: 0.38 MICROSIEVERT/HR.
- Distance 50 cm: 0.26 MICROSIEVERT/HR.



fig. 8: measurement at 0 cm, dial towards detector

With the case back towards the detector:

- Distance 0 cm: 0.85 MICROSIEVERT/HR.
- Distance 10 cm: 0.019 MICROSIEVERT/HR.
- Distance 50 cm: 0.015 MICROSIEVERT/HR.

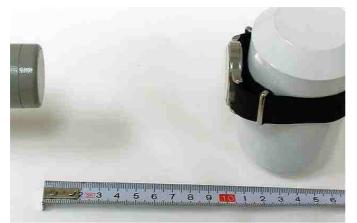


fig.9: measurement at 10 cm, dial towards detector



Fig.10: measurement at 0 cm, case back towards detector)

When the W.W.W.-watch is on top of the wrist and the radioactivity is measured at the opposite side of the wrist, we determine 0,35 microSievert/hr.

Please note that this is Gamma ray activity, first passing through the steel case back of the watch and then the full thickness of the 7-8cm wrist.



fig.11: Gamma radiation detection through the wrist)

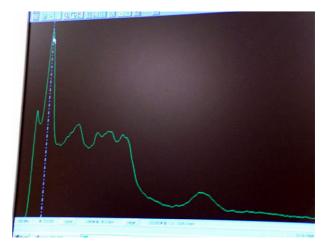


fig.12: spectrum of radioactivity emitted by Radium-226 and daughter nuclides

No radioactivity, exceeding the background radiation could be detected outside the ZINC SULPHIDE dialed K.M. pocket watch. THE MARK 11 and the OCEAN BUND, both with TRITIUM dial, did also not emit measurable radiation.

To test the presence of any possible trace of radioactivity, we have placed the K.M. pocket watch, dial towards detector, inside the lead container with the SODIUM IODIDE crystal.

- The scintillation detector counts 1137 counts per 120 seconds (569 counts per minute) as back ground activity.
- With the K.M pocket watch in place we registered over an 18 hr period a total of 600.203 counts.
- This total is also reached if the back ground radiation is calculated over 18 hrs: 614.500counts.

This means that no radiation outside the K.M. pocket watch could be detected.

RADIUM-226 transforms into several decay products which in turn emit radioactivity. The first decay nuclide is RADON-222 with a half-life of 4 days. RADON-222 disintegrates into POLONIUM-218 and ASTATINE-218.

POLONIUM-218 produces no Gamma rays and has a half-life of 3 minutes only. POLONIUM-218 is transformed into LEAD-214. This decay nuclide produces significant Gamma rays.

Thereafter 4 further daughter nuclides appear, all of them radioactive.

TRITIUM(H-3) disintegrates into HYDROGEN(H-2).

HYDROGEN is abundantly present on our planet especially bound to oxygen (O-2) in water, one of the essential compounds for life. The half- life of TRITIUM is less than 1% from that of radium-226:12.3 years.

ZINC SULPHIDE and SUPER LUMINOVA are non radioactive materials.

SUPER LUMINOVA is the current product used for luminescent dials by the watch industry, including by IWC. It is a non-radioactive phosphorescent compound developed during the early nineties.

The phosphorescent pigments work like light batteries. They are charged by daylight or artificial light to glow-in-the-dark for many hours. Its producer claims an up to 100 times better brightness compared to ZINC SULPHIDE.

Moreover, it is not subject to aging thereby preventing the fading that occurs with radioactive compounds.

Radioactivity entering the body is potentially hazardous. At extreme doses, it is lethal (atomic bomb. accidents in nuclear plants).

With lower doses infertility, genetic malformation or cancer may occur. No threshold of what doses should be safe can be given. In the U.S. it is estimated that the life time risk to develop cancer is 20.6 %.

Exposing a person to 100 MILLISIEVERT (20-30 times the back ground radiation) increases the cancer risk by 0,4%.

Starting or quitting smoking influences the cancer risk on a much more dramatic scale.

It should be emphasised that radioactive elements such as RADIUM-226 and TRITIUM are natural components on our planet.

Sources of natural radiation are cosmic rays, air, soil, water, building materials,

cigarette smoking, watching T.V. and flying at high altitude.

In Europe, it is estimated that the background radiation should not exceed 2000MICROSIEVERT/year or 2 MILLISIEVERT/year. This is equal to 200MILLIREM/year. In the U.S. the standard is with 3,0-3,5 MILLISIEVERT/year somewhat higher but differences per State exist, depending from the altitude where people live. Workers at the radiological or nuclear department in a hospital should not receive more than 2.0 MILLISIEVERT extra per year if they follow strictly the safety and protection rules.

We have found no significant radiation outside the IWC military watches equipped with a TRITIUM dial.

However, we found significant Gamma radiation emitted from a RADIUM-226 containing dial present in a 60-year-old IWC W.W.W. watch. We have to stress that this is not typical for IWC. In those days every producer used RADIUM-226 as it was the only available product.

With a maximum of 2,3 MICROSIEVERT/hr. the absorbed dose per year is 2,3x24x365 is 20.148 MICROSIEVERT/year or 20 MILLISIEVERT/year.

This is 7-10 times more than the average back ground radiation.

As such, this may cause serious concern. However, our findings have to be interpreted with caution.

While we could measure,2.3 MICROSIEVERT/hr. on the dial, only 0,85 MICROSIEVERT/hr. was found at the case back. This means that about 2/3 of the

Gamma rays are stopped by the steel case back.

In physics there is the "law of square".

If one doubles the distance between source of radiation and detector, the amount of radiation is not decreased by half but by 1/2x1/2 or a 1/4.

If one triples the distance the radiation is decreased by 1/3x1/3 or a 1/9.

This explains why at 50 cm from the dial we could measure only about 10% of the radioactivity measured at the dial.

Moreover, the different parts from the body have different sensitivity for radiation. Sensitive parts are the thyroid, the gonads, the small intestine and the bone marrow. Although a wrist watch is virtually in contact with bone, no bone marrow is present in the wrist of adults. The bone marrow is predominantly present in pelvis, vertebrae, shoulders, hips and ribs. Skin, muscles and tendons which are besides bone the other components from the human wrist, are remarkably resistant to radiation. Another reason to be careful with conclusions is the fact that we have only measured one watch containing RADIUM and it is clear that the concentration of RADIUM in the radio luminescent paint may differ considerably in a larger sample. Our results should therefore be considered as indicative, not as absolute.

As explained, it is completely justified that RADIUM-226 has been abandoned by the watch industry 40 years ago.

However, we do not believe that, based on rational facts, owners of an authentic IWC W.W.W. or early Mark 11 RADIUM dialed watches should have the dial removed for safety reasons.

The amount of time that the watch is on the wrist, the distance from the watch to sensitive organs and the radioactive resistance of the wrist, would justify to keep it original. Our view may be of interest for purist collectors, but of course, nothing is wrong in replacing a RADIUM dial for a TRITIUM one. Collectors should realise that they should not dismantle a RADIUM watch themselves and they should avoid storing multiple RADIUM watches in a cigar box in the attic to be discovered there by their grandchildren in half a century from now.

René Schwarz from IWC after-sales confirms that very few IWC watches containing RADIUM are seen in Schaffhausen for service.

If the dial is in good shape and the client wants to keep it, it is left alone. If restoration is necessary, the dial is not repainted with RADIUM-226 but with SUPER LUMILNOVA. Alternatively, it is removed and changed for a TRITIUM or SUPER LUMILNOVA dial.

Working on a watch with RADIUM is done in a special room and the Swiss health authorities on a regular basis control the responsible watchmakers.

ONCLUSION

Watches with RADIUM dials have to be handled with care and respect. Collectors should understand, at least for a part, what can be allowed and what should be avoided. The threat of radiation is often determined by emotional arguments rather than by scientific data.

Therefore, we would like to do a recalculation with the IWC W.W.W. emitting 20 MILLISIEVERT/year. If one considers that the wrist is at about 30-50 cm distance from our breast and abdomen, the radiation arriving there is reduced till about 10% or 2 MILLISIEVERT/year.

If one wears the watch during 3 months per year,8 hours a day, the total estimated whole body radiation is 1/4x1/3x2 MILLISIEVERT/year or 1/6 MILLISIEVERT/year. This low quantity of radioactivity justifies that we as purists like to keep the original dial.

If one still is worried, our advice is to send the watch to the place where the dial could safely be replaced: Schaffhausen.

September 2006



1.Paul Frame. **Radioluminescent Paint** Oak Ridge Associated Universities. April 2005.

2.*Health and Safety Executive Local Authorities Enforcement Liaison Committee(HELA) Hazards from luminised Timepieces in Watch/Clock Repair.* UK, Revision 2001,Review Date September 2005.

3.Ross Mullner. *Deadly Glow. The Radium Dial Worker Tragedy.* American Public health Association 1989.

4.J Kimball *Estimating Cancer Risks. Is there a safe dose of any mutagen or carcinogen?* Biology Pages, April 2006-09-19.

5. Konrad Knirim *Military Timepieces.* 150 years watches and clocks of German Forces.



We want to thank René Schwarz from IWC for his cooperation and advice as well as personnel from the DEPARTMENT OF NUCLEAR MEDICINE, Jeroen Bosch (Hospital's-Hertogenbosch, The Netherlands), <u>Greg Steer</u> (IWC Forum) Thomas Koenig (IWC Forum) and Konrad Knirim (author and specialist of German military watches).