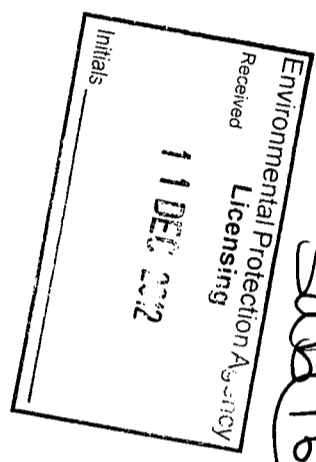


SUB(16)



10<sup>th</sup> Dec 2012

TO: E.P.A  
FROM: James Rountree  
Sellar  
Nobber  
Co. Meath

RE: Change of status re light hazardous waste at Indaver Incinerator  
Carranstown, Duleek, Co. Meath and increase annual tonnage by  
20,000 tons.

E.P.A. Licence No. WO167-03

Dear Sir/Madam,

I enclose a copy of any submission to the Bord Pleanala Oral Hearing  
1<sup>st</sup> - 4<sup>th</sup> October last for your information. A considerable amount of the content  
is directly relevant to E.P.A. and represents further elaboration to my initial  
submission and a copy of this is already sent to you. Please consider all my  
submission to Bord Pleanala is also to be treated as a submission to E.P.A.  
There is a European Court judgement (referred to) that requires this

I am adamant that left over paint and paint rinsings must be recycled and I  
have been looking around for a high value product that could be produced from  
recycled paint "CHASIS BLACK" paint is a good possibility. It retails at over  
€100.00 for 5 litres. Specification is that it has a high oil content and never fully  
dries out. It will scratch but will not chip or flake. It is resistant to heat in a similar  
way to "radiator paint" and to all road environment splashes. It is a binary paint  
i.e. a potent anti-corrosion chemical is added before use and must be used within  
6 months of mixing. Uses are in the motor trade and industry. It is highly  
recommended as an under-body anti-rust treatment for motor vehicles and has  
good rust penetration characteristics. (If suitable filter-masks are not available, it  
must be applied by brush). Surfaces do not have to be perfectly clean, but they  
must be fully dried out and this includes flake rust that could in many respects act  
as a sponge for moisture.

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Such a product would be an ideal outlet for paint recycling and there is scope for the promotion of a consumer friendly version for DIY motor vehicle and lawn mower, etc maintenance i.e. there is a currently unfulfilled market "niche" available but with the proviso that there are physical safety issues. A suitable ramp is needed with no jacks involved.

-----

On the issue of public health concerns about Incinerator emissions and Chromium in particular, Dr Martin Hogan from Employment Health Advisors Ltd. stated at the Oral Hearing that there are no concerns about Chromic Acid in the air at the low concentrations of Chromium emissions that the Indaver Incinerator at Dulceek is producing. He said that the issue is "DOSE". Comparison of exposure on the factory floor with attendant staff health monitoring is an entirely different matter to exposure of the general public and his views are contentious. There is a serious question here and the public interest must be served.

I enclose

1. Copy of submission to ABP Oral Hearing.
2. Photocopy of Text Book Chapter on Chromium.
3. Photo copy of reference (1950) from Encyclopaedia Britannica.
4. Copy of submission to ABP from Dr Hogan on behalf of Indaver for your information.

Please consider all material submitted by me for the Indaver licence revision.

Yours faithfully

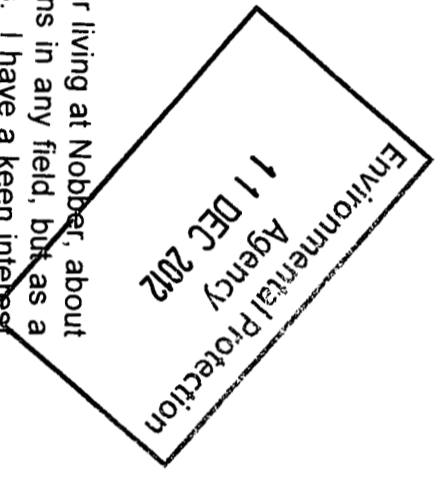
James Rowntree

046 - 905 2959

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Amendments to existing legislation - Increase kerage by 20,000  
cows + increase "light", keep down waste"

SUBMISSION  
FROM JAMES ROUNTREE  
SELLAR NOBBER  
CO. MEATH



My name is James Rountree. I am a dairy farmer living at Nobber, about 17 miles from the Indaver Plant. I have no qualifications in any field, but as a member of the public I am entitled to voice my concerns. I have a keen interest in health and a clean environment and you will note that I want to see various systems of gathering and analyzing health statistics compared on an ongoing basis. No one system should be depended on to the exclusion of others i.e. I went to see constant and continuous stational review with a variety of approaches because everyone knows that there are statistics and there are damned statistics. This is a serious matter of public confidence, evidenced by widespread subjective views that there is too much cancer, diabetes, asthma etc in the North East.

"I don't need to be an anthropologist to tell you that there is resignation and passive anxiety in the community and it is not there without reason, which of course should be inquired into, too. Indavers public relations flies in the face of this and is missing a very serious point that requires good social common arise.

Now, enough of that. We move on to an agriculture matter.

When a food scare arises there are two sections of the farming community. Those with the contamination problem proper and whose produce fails tests and the rest who need to guarantee that they do not have problem. To spot much a problem in the first place the Department of Agriculture and Food Safety Authority operate a SENTINEL POLICY and regularly test local produce but they do not observe one of the rules of environmental testing. (Anyone who says that food safety and environmental testing are separate issues is playing politics and flying in the face of public concern). The permission of the landowner and the reporting back directly of the detailed results is deficient and it is a rule of the proper recognition of environmental testing that the consent and subsequent information is available. This is something that needs to be discussed with the authorities. Question - who owns the information? It is very annoying that you can not see the laboratory certificate.

J.F.A. was advised to look for the establishment of a baseline study to help guarantee farm produce. This was good advice, but there is a problem that was not recognised at the time. Neither government or industry wants baseline study of farm produce because it interferes with the government/industry relationship. At earlier Oral Hearings I argued for an Agricultural baseline study. The authorities realised there were concerns but the baseline concept for farm

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produce was not taken on board and their was no improvement of the farmers position should a food scare arise i.e. dumping of produces and loss of income.

We do have a policy of traceability from farm level but it depends on confidence and it needs further development at processor and trader level. Even so, we are very proud of traceability systems, but market disruption is so much more extensive then a contamination problem proper.

So what is to be done? Technology has the answer. A good example is the DNA testing that now shows up spurious pork that is masquerading as Irish produce. Also, the African breed Zebu beef was shown up on sale in Irish restaurants. I think we must look to technology again so that any possible future food scare can be better managed.

I am putting forward a suggestion for discussion and consideration. We should have a scheme for graphing all undesirable chemicals and developed as a chemical fingerprint. If the stack output for sources of emissions is analysed and graphed and similar done for the other sources, a chemical analyst could review the produce graph and report the relative contributions of each of the emission sources and it does not matter that levels are below limit values, everyone should have confidence in the system. Technology has developed to a stage now that accurate readings at very micro levels are possible and readings of levels that are regarded as being of no consequence would be a better guarantee than the agricultural baseline that was advised earlier. The DNA testing I referred to was a world first and this could be another world first marketing aid.

Currently many vegetables producers around Drogheda are being charged annual fees for laboratory testing by supermarket and wholesale purchasers so that guarantees can be maintained that produce is free from contaminants. This is a good protection for the consumer. Co-Op and food processors also have their own laboratory facilities. Why not have a food ordinated scheme? Who will lead it? We could have an Irish standard that no one else could match? And could you imagine what that would do for public confidence?

Finally, should dioxin, etc contamination ever arise, then government must order the party responsible to re-imburse members of the farming community whose incomes are affected (even if government decision is to have precautionary dumping), because if they do not, then the necessity for the fingerprint graph scheme I have outlined will be overwhelming. Also, in view of Indavers good reports of low dioxin emissions, they should have no problem agreeing to this and they do pay insurance premiums should an industrial accident ever happen.

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For the record, I am just an ordinary I.F.A. member who speaks on my own behalf and these are just my ideas on this subject. They arise out of personal concerns that I have.

Now, I want to speak about the contribution of E.P.A. to the planning process. So far, it has been minimal and I am speaking in the context of the European Court of Justice (ECJ Case C – 50/09 dated 3<sup>rd</sup> March 2011) regarding the separation of the planning process and environmental licensing.

This refers to failure by Ireland to "Correctly Transpose Article 3 of Directive 85/337 into Irish Law and procedures. The principal detail among others in the judgement is the separation of the planning and environmental licensing procedures. As I see it E.P.A. and Bord Pleanála have not "properly convened" for consideration of this application and perhaps this planning application may have to be repeated again with the necessary compliance with the judgement.

In this light it is very disturbing that the experience and expertise of E.P.A. which is believable when you consider that all the Cr VI compounds are derivatives of Cr O<sub>3</sub> Chromium tri-oxide and all contain oxygen. If you dissolve Cr O<sub>3</sub> you get Chromic Acid H<sub>2</sub> Cr O<sub>4</sub>, Cr VI does not arise in biological circumstances. Only under thermal treatment.

Chromates and Dichromate's are the principal chemical you would expect and they are the main problem – toxic and carcinogenic. They are analogous to sulfates i.e. similar in many respects and are frequently isomorphous to sulphates i.e. similar in many ways and interchangeable. Please refer to Wikipedia downloads attached.

My problem with the chromates and dic-chromates arises from a reference in the Ephraim textbook that seems to make them even more dangerous. Chromates and dichromate's in an uncontrolled situation are mixed and the relative quantities of each is pH dependant. According to the Ephraim text book, further acid will produce polychromates, which decay, when moisture is added to form di-chromates and free chromic acid.

The underlined paragraph in the Ephraim textbook says to me that with pre scrubbed incineration gases which contain a variety of acids, possible 15-20% water vapour and when there is a Chromium spike that polychromates are produced when you incinerate paint with Chromium pigments. This is dangerous and could compromise the health and life of individuals. Furthermore, as Chromium is a trace element in all materials of organic origin, there has to be a concern about all incineration.

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The situation has masked all long by environmental degradation of all Chromium VI compounds to Chromium III. Obviously there has been a variety of cascade reactions and the one I have just outlined is only one of them. And so, no evidence of a build - up of Chromium VI in the environment has ever been noted from incineration.

If I am right to any extent in my concerns there is a major oversight on the part of government and industry here which was masked by the environmental degradation of the Cr VI to Cr III and of course, the total Cr figure is all that is asked for. Ephraim is the reference I have for this or rather, I should say my interpretation. There is no possibility of error, misprint or mistranslation and Ephraim and Noone are both authorities on chemistry. Am I correct in my interpretation? Am I correct that the interpretation of the underlined paragraph is suitably applied? And is there any grounds for my concerns? I insist that this is not to be an argument about evidence superceding the text book because if it is the Brussels authorities will have to be approached.

I am not in a position to speak about medical aspects of Cr VI. Please consult internet site, "National Library of Medicine Chromium Compounds H. S.D.E Database" 90 pages TOXNET DATA NETWORK.

The values of chemistry must be brought to bear on this project. The developer needs to be requested to show a chemistry spread - sheet showing the effect of incineration on the feedstock before the whole perspective and impact on the community can be properly understood. Otherwise we are in a dangerous information deficit scenario. The water decomposition detail outlined and chromate substitution for sulfates requires the non-incineration detail outlined the control and abatement of any other source of Chromium emissions.

I have no competence on the subject of chemistry but as a lay man I have read up as best I could and now I have outlined my concerns. It is difficult to find people who will speak on the subject. This raises further concern about how such issues are spotted and highlighted .... It will be an interesting subject for future historians.

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Dr Martin Hogan on behalf of Indaver at Bord Pleanála oral hearing 1st - 4th Oct 2012

**Dr Martin Hogan FRCPi FRCM AFOM**  
**Occupational Physician**  
**Specialist Registration No. 11908**

Employment Health Advisers Ltd, Heritage Business Park,  
Mahon Industrial Estate, Blackrock, Cork.

**Private & Confidential**  
Mr David McDermott,  
WYG Environmental and Planning Ireland Ltd,  
Nugroove Office Park,  
Nugroove Avenue,  
Rathfarnham,  
Dublin 14

23<sup>rd</sup> August, 2012

**RE:**

**Indaver Ireland Waste to Energy Plant,  
Carranstown, Duleek, Co. Meath**

Dear David,

Thank you for asking me to comment on the proposed change of use for the above facility. As you know, I was involved in the original application to An Bord Pleanála and I researched and wrote much of the human health section of the original EIS. I also gave evidence on human health to the An Bord Pleanála oral hearing. As part of the development of this application WYG consulted with me and provided the emissions from the proposed amendments to the facility and most importantly

I understand the new application is for a 10% or 20,000 tonnes increase in annual maximum waste accepted at the facility and the inclusion of additional EWC codes which includes suitable hazardous and non-hazardous waste. It also included extension of waste acceptance and dispatch hours and additional ammonia and fuel oil storage tanks, an additional effluent treatment and engineering percolation area and conversion of the temporary to permanent status of two structures.

In the original application, there had been a number of concerns expressed in the submissions to An Bord Pleanála and subsequently at the oral hearing with regard to concerns with regard to emissions from the then proposed facility. Some of these appear to be restated now.

I understand the facility has now been in operation for a number of months. I also understand from information provided by Indaver Ireland and WYG that emission levels have been well below permitted emissions as set out in the facility licence and

Environmental Protection  
Agency  
11 DEC 2012

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indeed at times, items such as dioxins have been below detectable levels. This is very much as had been predicted by the operators of the facility but had been doubted by some individuals and groups.

I see that the new application involves additional waste acceptance. I do also note that one of the issues was that the current waste being taken has a lower thermal value than was expected. I understand this may be due to the fact that there was a lower calorific value in the waste perhaps due to a higher than expected amount of putrescible waste.

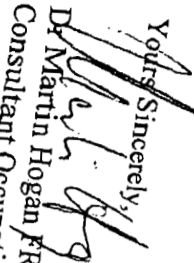
I do note that the actual incineration process and flue cleaning and energy recovering system will remain unchanged from those as built under the existing planning permission and waste licence and I understand there is no material alteration to emissions to the atmosphere from the stack and there are no increases or changes to emission limit values for stack emissions. This is confirmed in the Air Quality chapter of the EIS accompanying the current application.

I was asked to comment on the potential health effects of the additional capacity. In human health terms and environmental terms, it is not what goes into a plant which matters but rather what comes out or the emissions. I note that the emissions are well below permitted levels. It previously was assessed that even if emissions were up to the actual emissions from the facility have proved below those levels would in my mind reassure most individuals. While there may be some concern with the proposal to take in waste classified as hazardous, again in terms of human health impacts, it is any potential changes in emissions that might result that would be of significance and I do note that there is no expected change in emissions either being foreseen or allowed. In these circumstances there will be no human health effect from taking in this waste.

In these circumstances, I do not believe there is any likelihood of any significant impact on human health. I do not believe that in these circumstances it is necessary to revisit the assessment performed for the original EIS. I also do not believe there is any merit in considering baseline or other health assessments. These are notoriously difficult to organise and give very little usable information. I do not know of any location where they have been performed on similar sites where information has been gathered which has been of any practical uses.

In summary I do not envisage Human Health effects from the changes proposed in the application.

Yours Sincerely,

  
Dr Martin Hogan FRCP FRCPI FRCR  
Consultant Occupational Physician (IMC No. 11908)

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**CHRISTY, HENRY** (1810-1865), English ethnologist, was born at Kingston-on-Thames on July 26, 1810. From 1850-58 he travelled in Europe and America, studying ethnology. In 1858 the discoveries by Boucher de Perthes of flint implements in France and England were first held to have proved the great antiquity of man. Christy joined the Geological Society, and with his friend Edouard Lartet explored the caves in the valley of the Vézère. An account of the explorations appeared in *Comptes rendus* (Feb. 29, 1864) and *Transactions of the Ethnological Society of London* (June 21, 1864). He died, on May 14, 1865, leaving a half-finished book, entitled *Reliquiae Aquitanicae*, which was issued in parts and completed first by Lartet and, after the latter's death in 1870, by Professor Rupert Jones. Christy left his magnificent archaeological collection to the nation. In 1884 it was placed in the British Museum.

**CHROMATES AND DICHROMATES**, inorganic chemical compounds, or salts, in which the element chromium appears as part of the acid or "negative" component of the salt. Chromium trioxide, CrO<sub>3</sub>, commonly but incorrectly termed chromic acid, forms no crystalline hydrates with water, though its strongly acid aqueous solution is supposed to contain chromic acid, H<sub>2</sub>CrO<sub>4</sub>. The salts of this acid are known as chromates. Only normal salts, for example potassium chromate, K<sub>2</sub>CrO<sub>4</sub>, are known, which are analogous to and frequently isomorphous with normal sulphates. Acid or hydrogen salts, analogous to potassium bisulphate, KHSO<sub>4</sub>, are unknown. If an equivalent of acid be added to a solution of a normal chromate, the colour changes from yellow to orange-red, and from the mixture dichromates, for example potassium dichromate, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, alone can be isolated. If further equivalents of acid or, better, chromium trioxide, be added, the solutions become darker red and trichromates such as potassium trichromate, K<sub>2</sub>Cr<sub>3</sub>O<sub>10</sub>, and tetrachromates such as potassium tetrachromate, K<sub>2</sub>Cr<sub>4</sub>O<sub>13</sub>, are formed. The solid tri- and tetrachromates are decomposed on solution in water to form dichromates and free chromic acid.

Normal chromates are known of nearly all the stronger bases, both organic and inorganic, and are generally yellow. Ammonium, lithium, sodium, potassium, cuprous, cupric, rubidium, caesium, magnesium, calcium, zinc, cobalt and nickel chromates are soluble in water; strontium and the "rare-earth" chromates are sparingly soluble in water; mercuric chromate is decomposed by water, while silver, thallous, mercurous, cadmium, barium and lead chromates are insoluble in water. With the exception of cuprous, mercurous and magnesium dichromates which are unknown, all the metals forming soluble chromates also yield soluble red dichromates. Barium, lead and silver dichromates are known but are decomposed by water to form normal chromates and chromic acid.

chloride, CrCl<sub>3</sub>, volatile liquid, chloride of chromium unknown.

Though chromates are soluble in warm solutions, their salts or chromates are insoluble in water and form perchromates. It is accordingly that chromates are in chromates being in the same way as peroxide of chromium. The formula R<sub>2</sub>CrO<sub>4</sub> is used for the chromate of a metal R.

hydrogen peroxide is a weak oxidizing agent and on occasion it is used for the preparation of chromic acid. The blue color of chromates is due to the presence of the chromate ion. The blue color is due to the presence of the chromate ion. The blue color is due to the presence of the chromate ion.

hydrogen peroxide is a weak oxidizing agent and on occasion it is used for the preparation of chromic acid. The blue color of chromates is due to the presence of the chromate ion. The blue color is due to the presence of the chromate ion. The blue color is due to the presence of the chromate ion.

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DR FRITZ EPHRAIM

+ BY

DR P.C.C. THORNE (TRANSLATOR)

PRE WW II TEXT BOOK

## CHAPTER XVI

## METALLIC OXIDES—ACIDIC

*General methods of preparation—Stability—Manganates and permanganates—Ferrates, chromates, dichromates and polychromates—Halogen derivatives of chromic acid*

WHEN a metal has several oxides the basic properties of the hydroxides become less pronounced as the valency of the metal increases. Thus  $\text{Fe}(\text{OH})_3$  is a weaker base than  $\text{Fe}(\text{OH})_2$ , and  $\text{Sn}(\text{OH})_4$  is less basic than  $\text{Sn}(\text{OH})_2$ ; the decrease in basic power is shown by the greater hydrolysis of the salts of the higher hydroxide. When a certain limit in valency is reached the basic properties disappear almost completely and salt formation does not take place to an appreciable extent. The salts of  $\text{Mn}(\text{OH})_6$ , for example, hardly exist at all; and when oxides containing more oxygen than the neutral oxide are formed, they have definitely acidic properties. The oxides of hexa- and septavalent manganese give salts in which they function only as acid oxides. Another way of stating the result is to say that as the ionisation into OH ions becomes weaker, that into H ions increases. Further, if the metal is regarded as the positive part of the oxide and the oxygen as the negative part, the tendency of the oxide to approximate to the metal in its properties becomes less as the proportion of oxygen increases, and the compound thus becomes more electronegative. The higher oxides and chlorides of the metals are more volatile than the lower ones, as they tend to approach oxygen or chlorine in their behaviour.

Thus acidic oxides are formed only by those metals which can exert a high valency and thus combine with several oxygen atoms. The acidic tendency is sometimes shown even in the quadrivalent condition (Pb, Sn), but appears almost invariably in the quinquevalent and higher states of the metal. The metals in the right-hand half of the periodic table give the acidic oxides. The acids cannot always be isolated in the pure form, as they are frequently converted into the anhydride (chromic acid) or suffer extensive decomposition (ferric acid, manganic acid) or are polymerised (molybdic acid) when liberated from their salts.

The most important of these acids are: manganic, permanganic

and ferric acids; chromic, molybdic, tungstic and uranic acids; vanadic, niobic and tantallic acids. (The acids of the metalloids arsenic and antimony and of bismuth are discussed on pp. 626-630; those of the noble metals on p. 377.)

These acids show great variety in their properties; some are only known as salts and do not exist even in solution ( $H_2MnO_4$ ,  $H_2FeO_4$ ); others are known in concentrated solution, but decompose when an attempt is made to isolate them ( $HMnO_4$ ,  $H_2CrO_4$ ); others, again, exist in fairly concentrated pseudo-solution, but once isolated are only brought into solution again with great difficulty (molybdic, tungstic, uranic, vanadic, niobic and tantallic acids)—there is no reversible equilibrium in their solutions between the dissolved and the solid material. A similar set of differences exists in the salts of the acids; the acids of iron and manganese form only normal salts, chromic acid also forms salts in which a molecule of the anhydride is combined with the normal salt (anhydro-salts); while in the other acids of this class the effects of condensation and polymerisation are much more pronounced, and auto-complexes of high molecular weight and great stability are formed. This property is connected with that of forming heteropolyacids (cf. p. 405). It is obvious that comparisons between one group of these acids and another can seldom be drawn with advantage.

**Formation and Stability.**—The most important method of preparation is common to all these acids: the salts are obtained when a lower oxide of the metal is heated with alkali in the presence of an oxidising agent. When the acidic oxide is the most stable of the oxides of the metal it is formed when the metal itself or its lower oxides, hydroxides or sulphides are roasted in the air even when alkali is not present ( $MoO_3$ ,  $WO_3$ ,  $UO_3$ ,  $V_2O_5$ ,  $Nb_2O_5$ ,  $Ta_2O_5$ ). The oxides of Cr, Fe and Mn which are obtained in this way are not, however, the acidic oxides but lower oxides ( $Cr_2O_3$ ,  $Fe_2O_3$ ,  $Mn_2O_3$ ), and the higher oxides are formed only when alkali is present. The lower oxides can be fused with caustic potash or soda (or the carbonates) with admission of air, and the oxy-salts are formed, e.g.  $Cr_2O_3 + 2Na_2CO_3 + 3O = 2Na_2CrO_4 + 2CO_2$ . Oxidation is more rapidly and easily carried out if alkali nitrates or chlorates are used as oxidising agents instead of atmospheric oxygen, as they provide a more readily available supply of oxygen. It is remarkable that the oxidation of manganese to the manganate stage,  $K_2MnO_4$ , is incomplete; when a large excess of alkali is present a melt is obtained which contains only 2.6 atoms of oxygen per atom of manganese instead of the 3 atoms required by  $MnO_3$ . The mass has an intense dark green colour, and Sackur has shown<sup>1</sup> that it contains manganites, *i.e.* salts of the anhydride  $MnO_2$ , mixed with the manganate.

<sup>1</sup> *Ber.*, 1910, 43, 381, 448; 1911, 44, 777.

The potassium compound has the formula  $8K_2O \cdot Mn_2O_3$ , while that obtained from sodium salts is  $4Na_2O \cdot Mn_2O_3$ ; but it is more likely that solid solutions are formed, and not definite compounds, as there is no indication of an equilibrium between manganite and manganate—the same product is also obtained when potassium permanganate is heated alone or with alkalis. Baryta or lime can be used in place of caustic potash or soda. The formation of permanganate is interesting, for it is not a primary product of the oxidation of the lower oxides, but results from the decomposition and further oxidation of the manganate formed. When  $MnO_2$  is heated with alkali alone, manganate is produced at  $130^\circ$  by the decomposition  $3MnO_2 \rightarrow MnO_3 + Mn_2O_3$ , the  $MnO_3$  combining with the alkali. The  $Mn_2O_3$  is oxidised to  $MnO_2$  only at a red heat, when the above decomposition is repeated.

The manganate itself is also decomposed on further heating with formation of lower oxidation products and gives a definite dissociation pressure, which for  $K_2MnO_4$  is as follows:

Temperature . . . . .	$507^\circ$	$572^\circ$	$629^\circ$	$667^\circ$
Pressure of oxygen . . . . .	11	52.6	221	532 mm.

In a mixture of oxides of manganese and base, such as is obtained when permanganate is heated, the following apparently reversible dissociation pressures are obtained:

Temperature . . . . .	$505^\circ$	$560^\circ$	$600^\circ$
Pressure of oxygen . . . . .	50	129	400 mm.

Similar conditions obtain in the red melts formed by the fusion of iron compounds with alkali with access of air or addition of nitrate or chlorate. These contain ferrates, e.g.  $K_2FeO_4$ , but if formed at too high a temperature the ferrates, like the vanadates, are decomposed. When alkali vanadates are heated oxygen is given off with decrepitation, and if the residue is rapidly cooled a dark mass is obtained which contains vanadium in both the quadrivalent and quinquivalent states. On slow cooling, oxygen is absorbed and a clear red vanadate is obtained.

The normal chromates lose oxygen only at a high temperature, but the polychromates are more easily decomposed; thus, fused  $Na_2Cr_2O_7$  gives off oxygen at  $400^\circ$ . Even  $CrO_3$  is decomposed at high temperatures (p. 391). The salts of the other acids of this group (molybdic, tungstic, niobic and tantallic acids) can be fused without decomposition, or at least without loss of oxygen.

The above discussion indicates the best procedure in the preparation of these salts by the method of fusion with alkalis. When the anhydride of the acid is the commonest oxide of the metal (as with Mo, W, U, Nb, Ta, V) no oxidising agent need be added to the alkali. Niobates and tantalates are made in this way from the naturally occurring iron (manganese) niobate and tantalate (niobite, tantalite), and molybdates can similarly be made from lead molybdate (wulfenite), or from molybdenite  $MoS_2$  after roasting to  $MoO_3$ . Vanadates are also prepared from the natural heavy metal

PLEASE TURN TO PAGE 386  
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PARAGRAPH

vanadates, and tungstates from wolfram ( $\text{Fe, Mn})\text{WO}_4$  by roasting it in a furnace to render the iron insoluble and then fusing with sodium carbonate and leaching out the soluble sodium tungstate produced. In the manufacture of sodium uranate from pitchblende, as that salt is insoluble in water it is converted into soluble sodium uranyl carbonate by addition of sodium bicarbonate, and then precipitated as sodium uranate by addition of sulphuric acid. Oxidising alkali fusions are necessary for the production of the salts of chromium, iron and manganese, since only the lower oxides of these metals are found in nature. Pyrolusite is used as the raw material for the manufacture of manganese, and chrome ironstone, ferrous chromite,  $\text{Fe}(\text{CrO}_2)_2$ , for chromates.

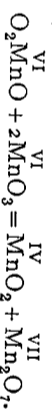
Only in a few instances can the acids be obtained directly by treatment of the ores with acids; but tungstic acid is formed when scheelite,  $\text{CaWO}_4$ , is treated with sulphuric acid, and niobic and tantalic acids can be prepared by fusing the minerals with potassium bisulphate. The acids remain as an insoluble residue contaminated with other substances, especially  $\text{TiO}_2$ , from which they can only be separated by conversion into the fluoro-salts (p. 292) and recrystallisation.

The method of oxidation in solution is sometimes employed for the preparation of these salts, but only for those made from lower oxides of the metal—iron, chromium and manganese. The reaction occurs more readily in alkaline solution, and ferric acid is not produced at all in acid solution as the free acid is unstable. Manganous and chromic compounds are oxidised by lead peroxide in nitric acid solution, a reaction which serves to detect minute quantities of manganese by the violet colour of the permanganic acid formed. Only chromium is oxidised by hydrogen peroxide and persulphates in acid solution, for permanganates are decomposed by excess of  $\text{H}_2\text{O}_2$ , thus providing a useful method of separating the two metals. In sulphuric acid solution the manganese is oxidised to the quadrivalent stage. Chromic salts are oxidised to chromates by permanganates.

In alkaline solution a great variety of oxidising agents can be used: hydrogen peroxide, persulphates, oxides of noble metals, hypochlorites, hypobromites, and other substances convert chromium salts into chromates, and similarly, but less easily, oxidise iron and manganese salts. Electrolytic oxidation is also frequently applied in alkaline solution for all three metals; an alkaline solution of the metallic salt or a suspension of the hydroxide in alkali is rapidly oxidised at the anode (which should be made of the same metal). Chromic salts are oxidised to chromic acid at the anode even in dilute sulphuric acid solution, and this method is used for the regeneration of the chrome liquors which are obtained when chromic acid is used on the large scale as an oxidising agent for organic substances. Permanganates and chromates are now usually manufactured by the electrolytic process, and even insoluble chromates like lead chromate (important as the pigment chrome yellow) can be made in this way; the solution of chromate or of chromic salt is electrolysed with a lead anode, and the lead chromate formed at the anode does not adhere if a little chlorate is added to the liquid. If no chlorate is added the anode

becomes coated with the insoluble chromate and the action stops, but the liberation of some chlorate ions prevents the formation of a continuous layer of chromate and thus exposes part of the anode to attack by the  $\text{CrO}_4$  ions.

**The Manganates and Permanganates.**—Manganic acid is probably a weak acid, while permanganic acid is a strong acid. *Manganic acid*,  $\text{H}_2\text{MnO}_4$ , is only known in the form of its salts and cannot be obtained in the pure state or even in aqueous solution; the anhydride  $\text{MnO}_3$  is equally unstable. *Permanganic acid*,  $\text{HMnO}_4$ , although unknown in the pure state, can be obtained in aqueous solution or as the anhydride  $\text{Mn}_2\text{O}_7$ . When an attempt is made to isolate manganic acid from solutions of its salts the acid decomposes into higher and lower oxidation products, thus:



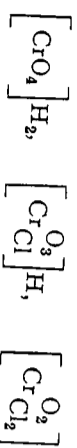
Hence, a precipitate of manganese dioxide separates out and the liquid becomes violet in colour owing to the permanganic acid formed. The latter can be reconverted into the green manganate by the addition of alkali, and on acidifying, the violet permanganate and the black precipitate are again produced. Even carbon dioxide suffices to set free the manganic acid from the manganate, and the  $\text{CO}_2$  normally present in the air is used technically to cause the transformation by blowing air through the solution from the green melt of manganate. Other acids, both strong and weak, act in the same way provided the acid has no reducing properties, e.g. hydrochloric acid cannot be used as it is oxidised to chlorine.

A solution of permanganic acid free from salts can be obtained by decomposing barium permanganate with the calculated quantity of sulphuric acid. It can be concentrated to contain 20 per cent.  $\text{HMnO}_4$ , but beyond that stage begins to give off oxygen. The concentrated solution decomposes readily into the *anhydride*  $\text{Mn}_2\text{O}_7$  and water, and as the oxide is somewhat volatile it can be recovered from the solution; it is most easily made by dissolving potassium permanganate in fairly concentrated sulphuric acid and warming to  $60^\circ$ . When the salt is added to the cooled concentrated acid, the oxide separates in oily drops—some dissolves in the acid to a green solution, and the rest forms a metallic-looking liquid below the acid. It is explosive, but not excessively so; it can be distilled on warming, giving a violet vapour, and sometimes detonates at a moderate temperature or when it comes into contact with oxidisable substances. Organic compounds are inflamed by it, and a black smoke of  $\text{MnO}_2$  is produced; in moist air the  $\text{Mn}_2\text{O}_7$  is slowly decomposed, the resulting oxygen being largely ozonised. The solution of  $\text{Mn}_2\text{O}_7$  in concentrated sulphuric acid is green, but on dissolving it in water the violet colour of permanganic acid is at once evident.

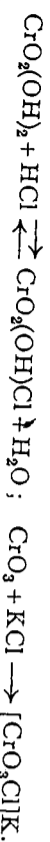
turn oxidises the "acceptor," that is, the sexavalent chromium is first of all reduced to the quinquevalent state, which exerts an oxidising effect, passing through the quadri- to the tervalent condition, the final product of the reaction.<sup>1</sup>

An obvious difference between chromic and permanganic acids lies in their behaviour towards hydrogen peroxide; whereas the latter undergoes reduction (p. 338), chromic acid can be oxidised to perchromic acid (see p. 419). Again, it is possible to obtain a chloride of chromic acid, chromyl chloride, from chromic and hydrochloric acids by removal of water before reduction of the  $\text{CrO}_3$  takes place, while the manganese acids only suffer reduction by hydrochloric acid.

**Chromyl Chloride, Chlorochromic Acid** and related compounds.—The oxygen atoms in chromic acid may be successively replaced by chlorine:



The displacement of one oxygen atom yields a monobasic acid, chlorochromic acid; and when both are replaced, a neutral body, chromyl chloride, is formed. Free chlorochromic acid is not known, but stable salts exist, produced from solutions containing chromic and hydrochloric acids and alkaline chloride; or alkaline chromate and hydrochloric acid give the salts on crystallisation



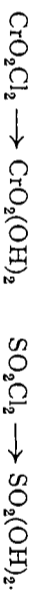
These compounds break down again if recrystallised from pure water, but can be obtained from solutions containing salt or acetic acid. They are well-defined reddish-yellow crystalline substances, and hold much water of crystallisation, in which they melt at a low temperature.

Analogous salts of a hypothetical fluorochromic acid, of a dark red colour, are also known. Bromo- and iodo-derivatives have also been described, but it is doubtful if they really exist, for it is likely that sexavalent chromium would be reduced by hydriodic acid, if not by hydrobromic acid as well.

The employment of larger quantities of HCl, in the presence of strong sulphuric acid (to absorb the water produced), drives the above reaction beyond the chlorochromate stage:  $\text{CrO}_4(\text{OH})_2 + 2\text{HCl} \rightleftharpoons \text{CrO}_2\text{Cl}_2 + 2\text{H}_2\text{O}$ . To prepare the chromyl chloride, a chromate is treated with alkaline chloride and strong sulphuric acid; the  $\text{CrO}_3$  and free HCl produced react with one another. Of course chromyl chloride may also be formed by the direct action of gaseous hydrochloric acid on chromium trioxide:  $\text{CrO}_3 + 2\text{HCl} \rightarrow \text{CrO}_2\text{Cl}_2 + \text{H}_2\text{O}$ . Chromyl chloride exists as a dark reddish-brown liquid, very like bromine, and its vapour also resembles that of bromine. It has a density of about 2, boils at  $117^\circ$  and freezes at  $-96.5^\circ$ . It is soluble

<sup>1</sup> Luther and Rutter, *Z. anorg. Chem.*, 1907, 54, 1.

without decomposition in carbon tetrachloride, carbon disulphide, nitrobenzene, antimony pentachloride and similar liquids; it is, however, rapidly hydrolysed by water:  $\text{CrO}_2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{CrO}_4(\text{OH})_2 + 2\text{HCl}$ . Thus chromyl chloride must be regarded as the acid chloride of chromic acid; the (OH) groups of the latter are replaced by chlorine. The substance belongs to the same class of compounds as sulphuryl chloride, the acid chloride of sulphuric acid:



Chromyl bromide and iodide appear to be just as incapable of existence as sulphuryl bromide and iodide. This property is made use of in the detection of chlorine in the presence of the other halogens. If a chloride is warmed with potassium dichromate and sulphuric acid, chromyl chloride distils over, and by absorption in alkali produces an alkali-chromate. When bromine is present, however, no such volatile chromium compound is produced. The existence of chromyl fluoride is very probable. A blood-red liquid of large vapour pressure has been obtained from a mixture of chromates, fluorides and strong sulphuric acid, which has not so far been definitely analysed, but may be  $\text{CrF}_6$ .

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