OFFICE OF MILITARY GOVERNMENT FOR GERMANY (U.S.)

THE ELECTRICAL AND TECHNICAL CERAMIC INDUSTRY OF GERMANY

SUPPLEMENTARY REPORT (HIGH DIELECTRIC CONSTANT INSULATORS)

by

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FIELD INFORMATION AGENCY, TECHNICAL

ABSTRACT

Additional information relating to previous FIAT and CIOS reports on high dielectric constant insulators and paramagnetic ceramics has been recorded.

PERSONNEL OF MISSION

Dr. Bennett S. Ellefson T.I.I.D. (FIAT)
Mr. Otto Guttmann T.I.I.D. (FIAT)

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INTRODUCTION

Objective:

The purpose of the investigation was to obtain more detailed information on the compositions and processes of manufacture of high dielectric constant insulators and ceramic paramagnetic materials.

Conclusion:

Some new data on the high dielectric constant insulators has been obtained as a supplement to previous reports. Of special interest is the additional information on thin ceramic processing.

Guide to Reader:

Reference will have to be made to previous reports (as listed in the Bibliography) in order to obtain a more comprehensive picture of the work done in the field of high dielectric constant insulators and ceramic paramagnetic materials. Supplementary information furnished in this report will refer specifically to these previous reports. New material has been reported under each of the separate topics discussed below.

MILLING

Reference:

Bibliography 1; Pages 8, 9.

" 2; Pages 3, 8.

" 3; Page 24.

" 4; Page 82.

Additional Information:

The advantage of very fine grinding of the raw materials in producing bodies of lower loss angle has been proven. Grinding times of 144 hours and a mill speed of 1.5 to 2.0 revolutions per second have been used by Dr. Rother. This long time grinding introduces mill contamination and it is recommended that a porcelain mill be used. It should have grinding balls made from a body composition similar to that used in the batch. When using flintstone balls in a Silex lined mill, the contamination can definitely be detected by an alteration of the electrical properties of the ceramic.

FIRING

Reference:

Bibliography 1; Page 9.

" 2; Page 9.

" 3; Page 24.

" 4; Page 82.

Additional Information:

The dimensional shrinkage in the firing of titania bearing bodies is in the order of 10 to 30%. The majority of the shrinkage takes place at temperatures between 1000 and 1200°C. A normal schedule used for the firing of titania bodies in the 0.5 cubic meter chamber of the 85 k.v.a. electric laboratory furnace is as follows:

Room temperature	to 500°C	5 hours
	500°C to 1000°C	7 hours
	1000°C to 1200°C	7 hours
	1200°C to 1320°C	2 hours
	Hold at 1320°C	3 to 5 hours
	Cool to 400°C	15 hours

Much of the dimensional shrinkage, etc., the range of firing 1000°C to 1200°C can be eliminated by prefiring the titanium oxides at 1200°C before mixing with other components. This prefiring has been found to be advantageous from the standpoint of reducing the failures in the press-forming operations.

THIN CERAMICS

Reference:

Bibliography 1; Page 70.

" 2; Page 3.

Additional Information:

A body designated by Dr. Rother as TA-1 and consisting of

Rutile S1053	81%
Rutile S1403	10%
Barium Carbonate	4%
Zircon Hydrate	5%

has been used for making very thin plates and thin walled tubing. This body has a dielectric constant of 95 to 100. In plates having a thickness of 0.6 mm., the loss factor at one megacycle is 4 to 8×10^{-4}; in 4.0 mm. diameter tubing with a 0.4 mm. wall the loss factor is 5×10^{-4}. Variations in the loss factor are introduced by the different binders used. In making the thin plates, 500 grams of the milled, dried and sieved TA-1 mass are mixed with 35 cc. of a one to one water solution of sulfite waste (from paper making). When dried this mixture is then passed through an ASTM 25 mesh sieve and pressed into thin plates. In making the tubing, 1500 grams of the milled, dried and sieved TA-1 mass is mixed with 500 cc. of a 5% solution of Tylose (a glue product). This mixture is extruded vertically and before being handled passes directly through the chamber of a small electric furnace operated at 900°C. Tubes 400 to 700 mm. in length, with diameters of 4.0 to 8.0 mm. and a wall thickness of 0.4 and 0.8 mm. respectively were exhibited by Dr. Rother. Because of the deleterious effect of the sulfite waste bonding agent on the electrical properties of the thin plates, other agents such as sodium phosphate had been studied. These mixtures had also been used for casting and plates as thin as 0.1 mm. had been prepared.

METALLIZING

Reference:

Bibliography 1; Page 11.
" 2; Page 9.
" 3; Page 24.
" 4; Page 82.

Additional Information:

Because of the poor expansion match between the silver and the ceramic body, the metal-ceramic bond from the standpoint of temperature has to be handled with care. This holds for soldering as well as later use. It has been found that a six hour firing at 400°C following the burn-in at 810°C is helpful in eliminating some of the failures. In soldering it is recommended that the temperature not exceed 200°C. The silvered ware is heated to 60° to 80° and a solder having a melting point of 142°C and a composition of Sn 47%, Cd 17% and the balance Pb is used.

LOW LOSS AND HIGH PERMITTIVITY CERAMIC BODY COMPOSITIONS

Reference:

Bibliography 1; Pages 12, 17.
" 2; Page 6.
" 3; Pages 22, 23.

Additional Information:

A typographical error exists in Table 1, page 12 of Bibliography Reference 1. Rutile S1043, should read Rutile S1403. In all cases where Rutile is mentioned without any further designation, it means that Rutile S1053 was used.

TITANIUM PEROXIDE AND TITANIUM OXIDES

Reference:

Bibliography 1; Pages 13, 14, 15.

" 2; Page 7.

" 3; Page 23.

" 4; Page 79.

Additional Information:

Titanium peroxide and the other titanium compounds were manufactured by I.G. Farbenindustrie A.G. at their Leverkusen plant. According to information supplied in a letter to Dr. Rother from Dr. F. Werther of I.G. Farben the titanium peroxide was produced by neutralization of titanium sulphate and precipitation with hydrogen peroxide. Rutile S1053 consists of Rutile crystals and has a specific gravity of 4.0 - 4.1. Its calcination temperature was 950 - 960°C. Rutile S1403 consists of homogeneous rutile crystals and has a specific gravity of 4.2. It had been calcined at 1050 - 1100°C. Rutiox consists of fine homogeneous crystals. According to the letter this material had been calcined at 930°C and had a specific gravity of 4.9.

X-RAY ANALYSIS

Reference:

Bibliography 1; Page 15.

Additional Information:

No report had been received by Dr. Rother on the X-ray analysis of the raw materials and the bodies made from them. From records listing the materials on which exposures had been made, over one hundred X-ray powder diagrams were made. The X-ray equipment was loaned to Dr. Rother by Professor E. Schiebold, Institute for Roentgenology, Leipzig. Miss Pettinger and Miss Träger of Professor Schiebold's department operated the equipment at Lauf, Pegnitz. The films were at Leipzig for analysis at the conclusion of the war and no further contact has been established.

DARKENING OF IRRADIATED TITANIUM BODIES

Reference:

Bibliography 1; Page 18.

Additional Information:

Professor Hilsch at the University of Erlangen has begun preliminary work on a fundamental investigation of this problem.

PARAMAGNETIC CERAMIC BODIES

Reference:

Bibliography 1; Page 18.
" 2; Page 3.
" 3; Page 24.
" 4; Page 79.

Additional Information:

A silicon carbide plate is used to support these materials during firing.

The soapstone used in the F11 body is a pure material from Spain. Samples of F7 and F16 had been submitted to Professor Falkenhagen, Technische Hochschule at Dresden, for measurements on permeability and permittivity. No data are available on these measurements. The body compositions are:

F7 Body

Fe_3O_4	78%
Iron powder	7%
Ordinary Clay	7%
Soapstone	8%

F16 Body

Fe_3O_4	50%
Blue Clay (Czechslovakia)	7%
Soapstone	43%

Crude measurements made on a more recent preparation F130 (containing 5% copper oxide) indicates a permeability value twice as great as that for F11.

Firing these pressed bodies to 800°C gives them enough strength to allow machining. Final firing temperatures of 1400°C and higher in a reducing atmosphere are required. The paramagnetic properties develop within a rather narrow temperature interval.

HIGH FREQUENCY RADIATION ABSORPTION

Reference:

Bibliography 1; Page 19.

" 2; Page 3.

" 4; Page 83.

Additional Information:

Composition 524 consists of:

Rutile S1053	90%
Cerium Carbonate	10%

This mixture was fired, powdered and then applied to metallic surfaces with an oil vehicle. At 30 cm. the reflection from such surfaces had been dropped to 25% of the value of the uncoated surface. Dr. Becker and Dr. Schmidt, Leipzig, contributed theoretical calculations on this problem.

CERAMIC LOADED PLASTIC FILMS

Reference:

Bibliography 1; Page 21.

" 2; Page 4.

" 3; Page 84.

Additional Information:

Composition of body 508 is:

Rutiox	4%

Bentonite	2%
Cerium Carbonate	10%
Bismuth Carbonate	4%

Data reported by the Eberswalde works of A.G. Schering indicate some interesting properties for the loaded film. The unloaded pure film (Triafol W) when heated to 80°C loses its moisture and the dielectric constant decreases. When heated further to 130°C the film shrinks and a capacitor constructed from such a film shows an effective increase in capacity due to the dimensional change. When allowed to stand at room temperature the capacity returns to its original room temperature value. A capacitor made from pigmented film has higher absolute values of capacity (dielectric constant of pure film about 3 and pigmented film about 20) but undergoes a similar cycle of capacity changes on heating (50% increase in capacity at 130°C). However it does not change from its high value at 130°C even though held for as long as eight hours at room temperature in a 54% relative humidity.

COEFFICIENT OF EXPANSION

Dr. Rother had made no measurements on the coefficient of expansion of the various bodies prepared. In the discussion with Dr. Schusterius at another target he stated that all of the commercially feasible titania bodies that he had studied had pretty much the same expansion characteristics. Titania-zirconia and titania-lanthania bodies have coefficients of expansion of the order of $8\text{-}10 \times 10^{-6}$ in the temperature range from 20°-100°C. In the same temperature range the value for steatite bodies fall in the range of $7\text{-}8$ c 10^{-6}.

USE OF ZIRCONIUM OXIDE

Reference:

Bibliography 1; Pages 12, 13.

" 2; Page 6.

Bibliography 3; Pages 21, 22.

" 4; Pages 77, 104.

Additional Information:

Dr. Schusterius stated that his work on zirconium-titanium oxide bodies was initiated in order to determine what replacement of the titanium ion (0.64 Angstrom radius) by the larger zirconium ion (0.86 Angstrom radius) could be effected and what influence such replacement would have on the electrical properties. He found a limited (15 to 20%) solubility at 1400-1500°C of the zirconium oxide in the titanium oxide. Dr. Schusterius had as yet not arrived at any completely satisfactory explanation for the changes in electrical properties which such an introduction of zirconium brings about. Bodies containing essentially pure TiO_2 have a value of dielectric constant of 80-100 and a large (800×10^{-6}) positive temperature coefficient of dielectric constant. When ZrO_2 is introduced to the limit of solubility the dielectric constant of the body is about 25 and the temperature coefficient of dielectric constant becomes highly negative (-300 c 10^{-6}). Dr. Schusterius did mention that it is interesting to note that there is less tendency of a zirconium-titanium oxide body to discolor on firing as compared to a relatively pure titanium oxide body. He felt that one might reason that since the lattice was strained by the introduction of the larger zirconium ion, it would be more reactive and hence have a greater affinity for oxygen.

USE OF LANTHANUM OXIDE

Reference:

Bibliography 1; Pages 12, 13, 15, 20, 21.

" 2; Pages 6, 7.

" 3; Pages 21, 22, 23.

" 4; Pages 77, 102.

Additional Information:

The basis for the original studies by Dr. Schusterius on the use of rare earths for the high dielectric materials was an attempt to find a commercial outlet for an excess by-product supply of rare earths produced by Auergesellschaft.

When mixtures of lanthanum oxide and titanium oxide are fired, a chemical compound is formed containing a one to one mol ratio of the two oxides. Such a body (one to one mol ratio) has a dielectric constant of about 35, almost zero temperature coefficient of dielectric constant and a very small loss angle. High firing temperatures (1400-1500°C) are necessary to bring about the compound formation.

USE OF TIN OXIDE

Reference:

Bibliography 4; Page 102.

Additional Information:

The basis for the studies by Dr. Schusterius on the tin ozide-titanium oxide bodies was to determine the effect of the substitution of the tin ion (0.74 Angstrom radius) for the titanium ion (0.64 Anstrom radius). A complete solubility of one oxide in the other in the form of a mixed crystal is possible in this system. With increasing tin content the dielectric constant decreases and the temperature coefficient of dielectric constant decreases. These bodies have not been found to be of any particular commercial significance since the electrical characteristic can be achieved by other more feasible combinations.

APPENDIX 1

List of German Personnel Interviewed

Name	Location	Address
Dr. Carl Schusterius	Kaiser Wilhelm Institut für Silikatforschung	Königshofen-Grozfeld Bavaria.
Dr. Franz Rother	Lutz and Co.	Lauf-Pegnitz.

APPENDIX 2

List of Targets Visited

Name	Location
Kaiser Wilhelm Institut für Silikatforschung	Loewenkeller. Königshofen-Grozfeld Bavaria.
Lutz and Co.	Doebrich and Heckel Buildings Lauf-Pegnitz.

APPENDIX 3

Bibliography

Related Reports Published by Allied Intelligence Agencies:

1. CIOS Report, File No. XXIX-31
   "Lutz and Company at Lauf, Pegnitz"
   by F/Lt. S. J. Bogars.

2. CIOS Report, File No. XXIX-48
   "Ceramic Developments of Dr. Rother,
   Lutz and Co." by Lt. Col. R. H. Ranger,
   Sig. Corps.

3. CIOS Report, File No. XXXI-22
   "Refractories in Turbine Blades plus
   Miscellaneous Applications" by Dr. S. S. Kistler.

4. FIAT Final Report No. 617, "The Electrical
   and Technical Ceramic Industry of Germany"
   by Dr. Ralston Russell Jr., JIOA.

The following patent applications have been made by Lutz and Co., Lauf Pegnitz during the years 1941 to 1944:-

Verfahren zur Herstellung von keramischen Werkstoffen
mit sehr hoher Dielektrizitätskonstante
10 Juni 1941 Aktenzeichen: L 104567 VI b/80b
Erfinder: Dr. Franz Rother.

Verfahren zur Herstellung von keramischen Körper mit
hoher Dielektrizitätskonstante
9 Juli 1941 Aktenzeichen: L 104827 VI b/80b
Erfinder: Dr. Franz Rother.

Keramischer Werkstoff für elektrische Anwendungszwecke
21 Juli 1942 Aktenzeichen L 108504 VI b/80b; 8/13
Erfinder: Dr. Franz Rother.

Mischkörpen mit erhöhter Dielektrizitätskonstante
10 März 1943 Atkenzeichen L 110 822 VIII b/21c
Erfinder: Dr. Franz Rother.

Verfahren zur Steuerung oder zur Vernichtung elektrischer Energie beziehungsweise elekstrischer Felder
20 Nov. 1943 Aktenzeichen L 113269 VIII a21/a4
Erfinder: Dr. Franz Rother.

Sperrschichtzelle auf keramischer Grundlage
27 Nov. 1943 Aktenzeichen L 113210 VI b/80b
Erfinder: Dr. Franz Rother.

Glimmeraustauschstoff
21 Dez. 1943 Aktenzeichen L 113450 VIII b/21c
Erfinder: Dr. Franz Rother.

Verfahren zur Vernichtung elektromagnetischer Felder bezw. elektrischer Signale
17 Jan. 1944 Aktenzeichen L 113524 VIII a21/a4
Erfinder: Dr. Franz Rother.

Verfahren zur Ortungsabwehr
15 März 1944 Aktenzeichen L 113985 XI 72g.

Verfahren zur Bekämfung feindlicher technischer Kamfeinheiten, beispielweise feindlicher Bomber-Geschwader.
22 Mai 1944 Aktenzeichen L 114520 XI 72i
Erfinder: Friedrich Mayer, Dr. Franz Rother, Dr. Nikolaus Lutz.

Anordnung zur teilweisen oder vollständigen Reflexion elektromagnetischer Wellen
24 Juni 1944 Aktenzeichen L 114902 VIII a21/a4
Erfinder: Dr. Franz Rother, Dr. Nikolaus Lutz, Dr. Friedrich Mayer.

Verfahren zur Erzeugung hochgespannten Gleichstromes
21 July 1944, Aktenzeichen L 115145 VIII d/21d
Erfinder: Dr. Franz Rother, Friedrich Mayer,
Dr. Nikolaus Lutz.

Keramischen Werkstoff mit extremen elektrischen
Eigenschafts werten
1 Sept. 1944 Aktenzeichen L 115457 VI b/80b
Erfinder: Dr. Franz Rother.

Elektrischer Wärmegerät für Heiz und Kochzwecke
3 Okt. 1944 Aktenzeichen L 115775 VIII c/21h
Erfinder: Dr. Franz Rother, Dr. Nikolaus Lutz,
Friedrich Mayer.

Verfahren zur Herstellung eines Filmes mit hohen
Dielektrizitätskonstante
19 Aug. 1941 Aktenzeichen L 110 833 VIII b/21c GR 2/30
Anmelder und Erfinder: Dr. Franz Rother.

Formstück für elektrische Isolationszwecke mit
verlängertem Kriechweg
1 April 1942 Aktenzeichen L 107316 VIII b/21c
Erfinder: Dr. Nikolaus Lutz, Dr. Franz Rother.

Plattenkondensator mit erhöhter Kapazitat
2 Okt. 1943 Aktenzeichen L 112780 VIII c/21g
Erfinder: Dr. Nikolaus Lutz, Johann Salomon.

Keramischer Mehrschicht kondensator
23 August 1944 Aktenzeichen L 115505 VIII c/21g
Erfinder: Dr. Nikolaus Lutz, Dr. Franz Rother.

Wickelkondensator für elektrische Zwecke
8 Mai 1943 Aktenzeichen L 111 419 VIII c/21g
Erfinder: Dr. Franz Rother.

Geformter Dielektrischer Mischkörper
19 Juli 1943 Aktenzeichen L 111241 VIII b/21c
Erfinder: Dr. Nikolaus Lutz, Dr. Franz Rother.

ERRATA TO FIAT FINAL REPORT NO. 617

The copy of the American report FIAT 617 which was reproduced photographically in this country for sale by H.M.S.O. contained over 200 mistakes. No attempt has been made to correct the numerous typographical errors such as Oarbide for Carbide and Frets for Frits on page 2. The major omissions of technical data are however listed below. It is regretted that the incorrect version was reproduced for sale purposes. A copy of the report corrected personally by Professor Ralston Russell Jr., the author, may be seen on application to the B.I.O.S. Information Section, 37, Bryanston Square.

P. 7 line 38 — 2-2.5% CR_2O_3.

P.23 line 8 — INSERT:

(d) Zirconia, Thoria, Spinel: These materials are ground and acid-treated in the same manner as alumina.

line 22 — After "Xylol" insert "or rubber latex".

P.41 line 21 — INSERT:

(c) Fraction III: 30 Kg of alumina 2)b are mixed with 18 liters of decanted wash water from 4)a for about 2 hours in a 30 Kg mill. The slip is passed through 3600 mesh (ca.A.S.T.M. 150 mesh) and then diluted with water to a viscosity of 100cc/10sec.

P.47 line 23 — 99.5% Al_2O_3.

line 39 — 23.8% - Siletz Kaolin (calcined 1500°c).

P.51 line 28 — INSERT:

Injection Molding: The injection molding equipment was purchased from Franz Braun A A.G. Zerbstein. Weighed quantities of the batch are filled into the cylinder which is heated to 118-123°C. The mass is injected through a special head (pressure of 13000-18000#) into a water cooled mold (40°C). The molded parts are removed after being under pressure 3 seconds, and the flash is removed by high speed grinding.

P. 52 line 1 — Delete Be insert "30° Be".

P. 70 last line — for example, 1500 amperes at 25 volts.

P. 78 line 37 — after "in the compoisition" insert "The identification of this constituent as Titanium peroxide is questionable".

P. 85 line 24 — For "1000-10000 uf" read "100-1000 uf and an auxiliary unit with a range of 1000-10,000 uf".

P. 93 line 14 — For "14% 1.0% -- Clay Substance (22% Plastic Clay) (75% Kaolin).

read "48% 1.0% -- Clay Substance (22% Plastic Clay) (78% Kaolin).

P. 96 — 8. Specific Heat-Kcal/Kgm°C 0.19-0.21 0.19-0.21

Delete 12. Power Factor, 20°C:
50cy x 10^6 - 10^7cy.

Insert 12. Power Factor, 20°C
(a) 50 cycles.
(b) 10^6 - 10^7 cycles.

P.100 line 37 — For $CaO.SiO_3$ read $CaO.SiO_2$.

line 39 — For ($CaO.MgO.SiO_2$) read ($CaO.MgO.2SiO_2$).

P.102 line 24 — After "following range of compositions
1) (90-99% - TiO_2
(1-10% - Fe_2O_3
2) (60-90% - TiO_2
(10-40% - SnO_2"

P.120 line 2 — For "NbC," read "NdC,".

P.121 line 15 — For "NbC" and "WC_2)" read "NdC" and "W_2C)".

P.122 line 18		Composition S1 is as follows: (also S2) 81.3% - Tungsten Carbide (WC) 18.2% - Titanium Carbide (TiC) 0.5% - Cobalt powder 100.0%
P.123 line 3		Delete "80 Kg." - substitute "The".
	lines 27 & 28	Delete two sentences and substitute "lined with Hartmetalle. Weighed charges and pressures of about 4000 #/in² are normally used. Mechanical presses fitted with multiple dies have been used satisfactorily".

8697/950/8.47/P.S.C./27.59.2.