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December 1972

ISBN 0 642 99517 6

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ABSTRACT

Uranium dioxide fuel pellets for water-cooled reactors are usually made by cold pressing and sintering UO_2 powders with or without an organic binder.

A wide range of binders was assessed and the most suitable was Cranco 253 (Poly-butylmethacrylate). Other binders such as polyvinyl alcohol, zinc stearate and Sterotex showed some promise, but further optimisation of their level and method of addition and of the debonding and sintering procedure is necessary.

National Library of Australia card number and ISBN 0 642 99517 6

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BINDERS; FUEL PELLETS; LUBRICATION; MICROSTRUCTURE; POLYACRYLATES; POWDERS; PVA; SINTERING; URANIUM DIOXIDE

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1. INTRODUCTION

Uranium dioxide fuel pellets for water-cooled nuclear reactors are usually made by cold-pressing and sintering. At the discretion of the fabricator, an organic binder and/or lubricant may be added to the UO_2 powder to facilitate pressing, or the powder may be pressed without any added pressing aid; in the latter case, die wall lubrication would usually be employed.

A study of the literature on UO_2 pellet fabrication does not allow an unequivocal choice to be made on the fabrication route or on the best type of pressing aid. For example, the large Westinghouse fabrication plant at Columbia, S.C., described by Smith (1970) operates on a binder-free route. In a review of Canadian General Electric fuel production methods, Fanjoy (1966) also described a binder-free route. In contrast, Canadian Westinghouse (Brown 1969) use a dry 'Sterotex' addition, and U.K. practice appears to have been based, for a long time, on the use of the binder known as 'Cranco' (Dawson and Sowden 1963). Other proposed organic aids include camphor-stearic acid (Fareeduddin et al. 1964), Carbowax 20 M (Winchell 1960), PVA-Sterotex (Burke et al. 1957), stearic acid, polyethylene glycol or paraffin (Spalaris 1959), and zinc stearate (Mogard and Nelson 1961).

An organic additive may have mainly lubricating properties during pressing (a lubricant), or it may serve mainly to increase the strength of the pressed compact (a binder). Some additives can be classed as binder-lubricants since they serve both functions. In this report the term 'binder' will be used throughout to denote a pressing aid irrespective of its prime function. This is in accordance with common usage.

The main potential advantages of the use of binders compared with the binder-free route are:

(i) Better lubrication during pressing reduces stresses in the pellet and fewer pellets subsequently crack.

(ii) Better lubrication reduces density gradients in the pressed pellets and reduces the hourglass taper in sintered pellets.

(iii) The pressed pellets, being stronger, are more suitable for automatic production line handling.

(iv) Generally faster pressing rates and lower reject rates can be achieved.

However, the use of binders has certain disadvantages, the most important being:

(i) Extra costs are involved in adding the binder, particularly if this

is done by wet-mixing then drying and granulating the mixture (e.g. by spray drying). The cost of the binder itself must also be considered.

(ii) While some binders are volatile in H_2 and can be removed during sintering (for example camphor, zinc stearate and Sterotex) many others need to be removed prior to sintering by mild oxidation. The usual debonding process is usually carried out in a separate debonding furnace or in a preheated zone of the sintering furnace, at 800°C in a CO_2 atmosphere.

(iii) Improper burnout procedures may result in carbon or carbide impurities in the pellets. Also burnout porosity may be introduced if the binder is not dispersed very uniformly.

For a pilot scale UO_2 pellet fabrication line which was set up at Lucas Heights in 1969-70, a decision was made in favour of the binder-free route. This line and the associated development work are described in a report to be published. The main reasons for setting up this line were to provide a facility for preparing fuel pellets for the Commission's research and development programme and for studying unit processes of fuel fabrication. While the choice of binder-free route proved a valid one for this line, the organic binder route was also studied. The objective was to recommend a suitable binder or binders for a possible future fabrication plant incorporating a large amount of automatic production line handling, where a particular requirement would be strong and abrasion resistant pressed pellets.

In this report, the work on binder additions leading to the recommendation of one binder is described.

2. PLAN OF THE STUDY

The study was carried out in stages, referred to as Stages I, II, III and IV. In Stage I six common additives for UO_2 were assessed to select the most attractive types for further detailed investigation. In Stage II the percentage addition and burn out procedure in CO_2 were investigated for a smaller range of additives, and the sintered properties were assessed. Debonding conditions in CO_2 and moist N_2-3 Vol.% H_2 were studied in Stage III for the same additives, the main objective being to optimise the debonding procedure in CO_2 and to determine the feasibility of combining burnout and sintering into one operation. Finally, in Stage IV a comparison was made on a somewhat larger scale of pellets fabricated with and without the two most promising binders, to study reject rates.

3. STAGE I - PRELIMINARY BINDER ASSESSMENT

3.1 UO_2 Powder

The UO_2 powder used in Stage I was an 'Eldorado' Ceramic Grade batch having the properties shown in Table 1. This batch of powder, when die pressed without binder addition and sintered, always gave sintered pellets with longitudinal cracks. An extensive investigation was made of the powder processing variables but cracking was not eliminated. This problem was tentatively attributed to the high oxygen/uranium ratio in the powder.

3.2 Fabrication Procedure

3.2.1 Mixing

The binders used, the methods of addition, and concentrations are shown in Table 2. Water was included in the list because it increases internal lubrication and allows easier pressing for most ceramic powders. Terraza, Cerrolaza and Aparicio (1958) have shown that increased sintered densities in UO_2 compacts can be obtained with water additions. Each additive was mixed with 3 kg of UO_2 powder in a sigma-blade mixer. Those added in solution were dried while mixing to ensure uniform dispersion of the additive. Each batch was divided in two, one half being precompacted and granulated and the other granulated without precompaction. Fifteen pellets from each half of each batch were pressed with and without stearic acid die wall lubrication.

3.2.2 Precompaction-granulation

The dry powders were placed in closed end thin latex tubes, evacuated with a laboratory water pump, tied at the open end and isostatically pressed at 10,000 lbs/in^2. A two stage granulation procedure was used. The isostatically pressed powder was first mechanically granulated to pass through a 14 mesh sieve. The -20 +100 mesh fraction was then collected by hand sieving and the oversize was returned through a 20 mesh granulator and again resieved to collect -20 +100 mesh. The total -20 +100 mesh fraction collected was approximately 75% of the original amount of powder. A comparison of the flow characteristics of each powder was obtained by filling a brass funnel (having a ¼ inch diameter discharge orifice) and measuring the time to empty.

3.2.3 Automatic pressing

The powders were pressed at pressures of 10, 15 and 20 tons/in^2 in a double acting, hydraulically operated press. The die (0.702 in. bore) was manufactured from steel hardened to 68-71 Rockwell C and ground with a 0.009 in. taper on diameter over the last one inch of bore. The die wall was lubricated by injection of a measured amount of saturated stearic acid-trichlorethylene solution through the lower plunger into a felt wiper at each stroke. The green

strength of pressed pellets from each batch was compared by placing pellets axially under a hydraulic press and increasing the pressure at 25 lb/in^2 per sec until the pellet crushed. The applied pressure per unit area to produce crushing was an indication of the relative compressive strength of the pellets.

3.2.4 Debonding and sintering

Pellets from each powder and pressing condition were sintered with and without a debonding treatment. Debonding was carried out in a 6 in. diameter x 4 ft long stainless steel tube, closed at one end and with a removable flange at the other. The pellets were placed in alumina trays to a maximum distance of 18 in. from the closed end and heated in a muffle furnace to give a uniform temperature of 800°C throughout the pellet trays. The pellets were heated at 120°C per hour, maintained at 800°C for 4 hours, and cooled to room temperature in 24 hours. Throughout the entire heating and cooling cycle, CO_2 was passed through the tube.

Pellets prepared under all conditions were sintered in a continuous pusher furnace in a hydrogen atmosphere. The total time through the furnace was 40 hours and the pellets experienced a maximum temperature of 1500°C or 1600°C for 4 hours.

3.3 Results and Discussion of Stage I

The following observations were made:

(i) Die wall lubrication was necessary in all cases, except for the powders containing 1 and 2 wt.% Sterotex, to prevent chipping and cracking during ejection from the die.

(ii) Precompaction before granulation gave powders with better flow characteristics compared with powders granulated without precompaction.

(iii) Except in the case of water, zinc stearate and 0.2 wt.% Sterotex, debonding was necessary to prevent severe cracking and distortion during sintering.

Tables 3 and 4 compare the results obtained from pellets pressed with various binder additions using precompacted-granulated powders, debonded in CO_2. The conclusions drawn from these Tables were:

(i) Binders which show little effect on sintered density at the levels studied are PVA, zinc stearate, Sterotex and Carbowax.

(ii) Compressive strength of pressed pellets is increased with paraffin wax and Carbowax whereas Sterotex tended to decrease compressive strength.

(iii) Microstructures were unaffected with binders added in solution; dry

addition (of PVA and zinc stearate) gave burnout porosity (Figure 1).

(iv) Pellets containing zinc stearate and PVA gave crack-free pellets after sintering.

Using 'freedom from cracking' as the most important criterion, the most suitable binders were zinc stearate and PVA; zinc stearate gave similar results in the directly sintered (not debonded) pellets. Residual carbon was not detected in the debonded PVA pellets whereas a trace of zinc remained in the debonded zinc stearate pellets. However, the microstructure of sintered pellets pressed with these two binders show large pores due to binder burnout For PVA these pores could probably be avoided by addition of the binder in aqueous solution. Liquid addition of zinc stearate is difficult because it is insoluble in most common solvents, although (Chattergee and Patit 1962) report that it has approximately 12% solubility at 35°C in a solution of chloroform containing propylene glycol with secondary amines such as diethanoamine. Zinc stearate was not evaluated further in this assessment mainly because of the undesirability, in principle, of introducing an inorganic contaminant into the pellets. Another problem was the condensation of zinc in the inlet end of the furnace which on a large scale would present operational difficulties.

PVA was selected from the preliminary assessment for a more detailed investigation in Stage II using aqueous addition in preference to dry powder addition.

4. STAGE II - COMPARISON OF PVA AND TWO GRADES OF CRANCO

4.1 Materials and Powder Preparation

The binders and levels studied are shown in Table 5. In addition to PVA, two grades of 'Cranco Ceramic Medium' Nos. 82 (inflammable) and 253 (flash point 253°C) had been obtained for study in Stage II. Cranco (poly-butylmethacrylate in dibutyl phthalate) is soluble in acetone or trichlor-ethylene; acetone was used as the solvent in Stages II and III and trichlor-ethylene in Stage IV. The UO_2 powder used in this stage was a micronised blend of batches CE80-90 prepared by tray-calcination and reduction. The surface area was 4.1 m^2/g and the O/U ratio 2.09. The powder was generally difficult to press into crack-free pellets without a binder addition.

The powders were processed to the end of the drying stage as in Stage I. However the fabrication procedure was shortened (to eliminate precompaction) by passing the dried powders through a 20 mesh sieve and resieving to collect the -20 +100 mesh fraction. Pellets were pressed from this fraction at 20 tons/in^2 with double ended pressure. The die had the same internal diameter as that used in Stage I but the exit taper was 0.007 in. (on diameter) over the last

1 inch of bore. Fifteen pellets were pressed from each powder batch.

4.2 Abrasion Tests

The compression test used in Stage I gave no measure of the abrasion resistance of pellets, and three simple tests were devised to obtain some indication of differences in chip and abrasion resistance as a function of binder type and concentration.

Test 1

One pellet of each type was placed in a thin latex tube which was evacuated and sealed, and then placed in a Syntron feeder. The pellets ascended the spiral track of the feeder to the top where a deflection plate dropped them approximately 6 in. on to the base of the feeder. The feeder automatically returned them to the spiral track. Cycling in this manner was carried out for half an hour after which the weight loss due to chipping was determined on each pellet.

Test 2

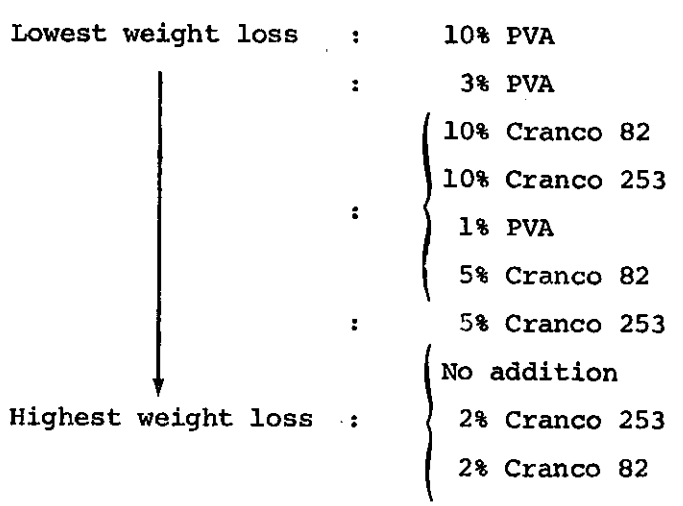
One pellet from each composition was placed in a plastic bottle and the bottle containing the pellets was placed on the base of the Syntron feeder and vibrated for 15 min. The weight losses due to abrasion were determined on each pellet.

Test 3

One pellet of each type was placed in a plastic bottle and all were tumbled together on ball mill rolls for 5 min and the individual weight losses recorded.

The results of Tests 1 to 3, given in Table 6, show that:

(i) For each binder the weight loss in each test decreased with increasing binder content as follows:



(ii) The above order was fairly consistent in all three tests.

4.3 Debonding and Sintering

Three pellets from each composition were debonded by heating in CO_2 to 800°C for 4 hours in a 2.5 in. diameter tube furnace (heating rate 400°C/hr). The CO_2 atmosphere was maintained during cooling until the pellets reached room temperature. The weight losses found on debonding are shown in Table 7.

Both debonded and as-pressed pellets from each composition were sintered in the continuous pusher furnace (H_2 atmosphere) for 4 hours at 1600°C; the sintered weight losses and sintered densities are also shown in Table 7. The conclusions were:

(i) Cranco appears to be removed with the debonding treatment; in all cases the percentage weight loss above 800°C during sintering is similar to that of the pellets with no additive. PVA is only partially removed in the debonding since the weight loss above 800°C is higher than with no additive (particularly at the 10% level).

(ii) Additions of up to 10 wt.% Cranco 82, when debonded, have little effect on sintered density; under similar conditions 10 wt.% of Cranco 253 showed a decrease in sintered density. PVA reduces sintered density at 3 wt.% addition and very markedly at 10 wt.%.

(iii) Additions of 5 and 10 wt.% Cranco 253 and 85 and 1 wt.% PVA give crack-free sintered pellets. Cracks were present in pellets containing more than 1 wt.% PVA.

(iv) Hourglass taper was highest with the three PVA additions.

4.4 Summary of Stage II

Excellent abrasion resistance was obtained with PVA at the 3 and 10 wt.% levels of addition, but the debonding procedure chosen does not appear to be satisfactory for complete removal of PVA and could account for cracking at the 3 and 5 wt.% levels. No attempt had been made to optimise the debonding procedure, which could affect the behaviour of PVA. An unattractive feature of PVA was the large hourglass taper due to variation in green density along the axis of the pellet; this was attributed to high inter-granular friction with this additive compared with Cranco, which apparently gave some internal lubrication.

Cranco 82 and 253 both gave good abrasion resistance at the 3 and 10 wt.% levels, and the burnout procedure was satisfactory; the sintering results were excellent. It was expected that even higher additions of Cranco would still burn out without trouble and this aspect was studied in Stage III.

5. STAGE III - OPTIMISATION OF DEBONDING PROCEDURES FOR CRANCO AND PVA

Organic binders are usually removed from UO_2 pellets by heating in CO_2 at

a temperature of approximately 800°C and this was the procedure adopted in Stages I and II. However, it had been shown (Adams and Stuart, private communication) that a moist sintering atmosphere of N_2-3 Vol.%H_2 substantially reduced the sintering temperature of UO_2 and it appeared likely that effective debonding may be achievable in this atmosphere; an added attraction was the possibility of combining debonding and sintering into one cycle. Debonding in these two atmospheres was examined in detail, by studying firstly the decomposition of the dry powdered binders and secondly the removal of the binders from pressed UO_2 pellets.

5.1 Decomposition of Dry Powdered Additives

PVA and Cranco 82 were studied, Cranco 82 being the less volatile of the two types of Cranco. Dried pulverised Cranco and PVA powders contained in a borosilicate glass U-tube were heated in a small vertical furnace. In experiment A, the sample was held for 1 hour at each temperature before proceeding to the next temperature. In experiment B, the samples were heated to 700°C in 2 hours and held for 3 hours.

A summary of the results is given in Table 8. These results show that the carbonaceous deposit is not as easily removed from either additive in moist N_2-3 Vol.%H_2 as in CO_2. Although these tests were carried out on granules and not thin films (as they would be present in fuel pellets), the same trends in removal of the binder would be expected. However, the possibility remained that the moist N_2-3 Vol.%H_2 atmosphere might give effective debonding at higher temperatures during a hypothetical combined debonding-sintering cycle, and this aspect was studied later.

5.2 PVA and Cranco Additions to UO_2 Powder

The powder used was similar to that in Stage II (CE92-93; surface area 3.8 m^2/g and O/U ratio 2.087). 3 and 5 wt.% PVA and 10 and 15 wt.% Cranco 253 and 82 were added and the powders were prepared as in Stage II. Granulation was done without precompaction, and pressing was in the automatic press in a steel die with an exit taper of 0.009 in. (dia) over the last 1 inch of bore. Debonding temperatures were within the range 600-1000°C in CO_2 and moist N_2-3 Vol.%H_2; direct sintering in N_2-3 Vol.%H_2 was studied only at 1400°C.

5.3 Abrasion Tests

The results of abrasion tests, carried out as in Stage II, are shown in Table 9. No significant difference was found between the two types of Cranco in these tests. The weight loss from PVA in Test 3 was considerably greater than in Stage II (Table 5). However, compared with pellets containing no additive these pellets showed a marked increase in abrasion resistance.

5.4 Debonding and Sintering in Moist N_2-3 Vol.%H_2

Debonding in moist N_2-3 Vol.%H_2 was carried out in a small laboratory tube furnace by passing the N_2/H_2 mixture through water in a gas bubbler at a rate of 200 cm^3/min. Two debonding temperatures, 850 and 975°C, were used and maintained for 4 hours. The debonded pellets were then sintered in H_2 at 1600°C. Table 10 summarises the results. Pellets were also sintered in the moist N_2-3 Vol.%H_2 atmosphere at 1400°C for 2 hours with no prior debonding treatment other than the normal heating up period; a summary of the results is given in Table 11. The amount of unremoved binder after debonding in moist N_2-3 Vol.%H_2 was estimated by comparing the weights of pellets containing binder after debonding with the weight of similar binder-free pellets; these estimates are given in Table 12. Table 12 also includes the results of debonding at 975°C with an increased flowrate (250 cm^3/min) compared to the normal flowrate of 200 cm^3/min.

The main conclusions drawn from Tables 10, 11 and 12 are summarised as follows:

(i) Debonding in moist N_2-3 Vol.%H_2 gives rise to severe cracking in the sintered pellets.

(ii) Sintered densities are low in both the debonded and directly sintered pellets compared with pellets with no additive.

(iii) The low sintered densities obtained with the two Cranco binders do not appear to result from incomplete removal of the binder during debonding.

(iv) On the other hand, PVA is incompletely removed by moist N_2-3 Vol.%H_2 and this probably explains the low sintered densities and cracking with this additive.

5.5 Debonding in CO_2

Similar debonding studies were carried out in CO_2 at temperatures of 600, 800 and 975°C using flowrates of 200 and 250 cm^3/min. Table 13 presents a summary of the sintering results and Table 14 gives the estimated percentage of unremoved binder (deduced as in Section 5.4). These results show that:

(i) Sintered pellets containing 3 and 5 wt.% PVA were cracked under all debonding conditions (as expected from the results of Stage II, Table 7) and showed a significant decrease in sintered density.

(ii) Both types of Cranco up to 15% additions were removed in CO_2 at 800°C; sintered densities of pellets containing these additions were not significantly different from those of pellets containing no additive. No significant difference is apparent between the two types of Cranco.

(iii) Cracking in the sintered pellets was noticeably less with the Cranco additions than in the pellets with no additive.

5.5.1 Analysis for residual carbon

The carbon content in sintered pellets containing 10 and 15 wt.% Cranco 253 and Cranco 82 and 5 wt.% PVA was found by chemical analysis to be less than 5 ppm in each case and was similar to that in binder-free pellets. Complete removal of the PVA must occur during sintering, since some residual material was present after debonding.

5.5.2 Microstructure

Sintered pellets containing Cranco 253 and 82, debonded at 800° and 975°C in CO_2, showed microstructures identical to otherwise similar binder-free pellets. Figures 2 and 3 respectively show the sintered microstructure (1600°C) of UO_2 containing 15 wt.% Cranco 82 debonded at 800°C and of a binder-free pellet. The microstructure of pellets containing 5 wt.% PVA showed a porous structure containing large voids (Figure 4), correlating with the lowered sintered densities. The voids are possibly due to swelling of the PVA during debonding.

5.5.3 Hourglass taper

Debonding and sintered pellets containing Cranco 253 and 82 at a density of 10.6 g/cm^3 had an average hourglass taper of 0.003 in. diameter compared to a taper of 0.005 in. for binder-free pellets at a similar density.

5.6 Summary of Stages I, II and III

Binder additions of PVA and Cranco 253 and 82 were found to markedly increase the abrasion resistance of green UO_2 pellets. Debonding studies showed that PVA binder additions greater than 1 wt.% were incompletely removed in CO_2 and moist N_2-3 Vol.%H_2 at up to 975°C; however, after sintering residual carbon was negligible even at the higher levels. Above the 1 wt.% level PVA decreased sintered density and gave rise to severe cracking. Green pellets containing 1 wt.% showed compressive strength and abrasion resistance similar to pellets containing 10 wt.% of either grade of Cranco. A particularly undesirable feature of PVA, even at 1 wt.% addition, was a large hourglass taper of 0.007 in. or greater (on diameter) in the sintered pellets, which would necessitate excessive material removal by centreless grinding. The large hourglass taper is thought to be associated with hard powder granules which offer a high resistance to deformation on pressing and this explanation is supported by Figure 4, in which granule outlines are apparent.

Cranco additions of up to 15 wt.% are removed in CO_2; they have no effect on final density and the number rejected, due to cracking, is less than with

PVA or binder-free pellets. The average hourglass taper of 0.003 in. (on diameter) of pellets with both Cranco additives was slightly less than that of binder-free pellets (0.005 in. on diameter). Cranco additions of greater than 10 wt.% gave no worthwhile increase in abrasion resistance or benefit in pellet handling and 10 wt.% was considered the optimum. The most effective debonding treatment was in CO_2 within the temperature range 800° to 1000°C; the upper end of the range was found to give harder pellets with easier handling benefits in subsequent stages. Direct debonding and sintering was not successful in moist N_2-3 Vol.%H_2.

Both Cranco types were selected in preference to PVA for larger scale investigation in Stage IV, to ensure that the results in Stage III could be reproduced with larger batches. In Stage IV, Cranco additions of 10 wt.% were used and debonding was carried out at 975°C in CO_2.

6. STAGE IV - LARGER SCALE COMPARISON BETWEEN CRANCO 253 AND 82 AND BINDER-FREE POWDER

6.1 Equipment

Prior to commencing this stage, a vertical stainless steel rotating blade mixer was constructed. This was designed to eliminate the tendency for non-uniform dispersion of the additive which occurred in the sigma blade mixer unless the material accumulating between the blade was fed back manually into the mix at frequent intervals. In the new mixer the whole batch was constantly stirred during drying, and additive separation was eliminated. A larger debonding furnace was also constructed to handle 20 pellets per batch. A metered gas flow was passed through the 3 in. diameter work tube, into which the pellets were inserted on an alumina tray.

6.2 Materials and Powder

The UO_2 powder was CEl16-120, of surface area 2.6 m^2/g and O/U ratio 2.11. Cranco 253 and 82 were added in trichlorethylene solution at the 10 wt.% level; the non-flammable solvent (previously acetone) allowed greater safety when handling large volumes. The dried powders were granulated to -22 mesh, and their pour and tap densities in this condition are shown in Table 15.

6.3 Pressing

The powders were pressed automatically at 20 tons/in^2 in a die with a taper of 0.009 in. on diameter over the last one inch of bore. Binder-free pellets were pressed with stearic acid-trichlorethylene lubricant and pellets containing binder were pressed both with and without die wall lubrication. Pellets from the powders containing binder ejected less freely than when

pressed without die wall lubrication and had rougher surfaces than when lubricant as well as binder was used.

The edges of all Cranco pellets were perfectly formed and very sharp whereas without binder slight chipping and more rounded edges were obtained; all the pellets were examined under a low power optical microscope and no cracking was apparent. Table 14 shows the effect of pressing with and without lubrication on the green density of the pellets.

6.4 Sintering Results

The pressed pellets containing Cranco 253 and 82 were debonded in CO_2 (flow rate 500 cm^3/min, 975°C for 1 hr) and both these and the binder-free pellets were sintered in H_2 at 1500°C for 4 hrs. The identity of the debonded batches was maintained during sintering, to assess batch to batch variations which might occur in the sintered pellets due to debonding. Table 16 gives an analysis of the results. Pellets containing any crack visible under low power optical magnification after centreless grinding, were rejected.

Cracking in the Cranco pellets occurred in the debonding stage but in all cases the cracked pellets were sintered to determine the overall reject rate. The main conclusions drawn from the results in Table 16 were:

(i) The lowest reject rate obtained in the sintered pellets was with Cranco 253.

(ii) There was no significant difference in sintered density between binder-free pellets and pellets containing Cranco 82 or 253 debonded at 975°C in H_2.

(iii) No edge chipping was evident with the pellets containing Cranco binders whereas all binder-free pellets were chipped.

(iv) The variable percentage of rejects indicated some batch to batch variation in debonding.

The O/U ratios of pellets from each powder were less than 2.002 and the residual carbon content was less than 5 ppm.

6.5 Fines from Powder Granulation

The -100 mesh fraction from the powder granulation stage is unsuitable for automatic pressing. The dry Cranco binders (i.e. polymerised) are insoluble in trichlorethylene and this relatively coarse granular material recycled into the mixing stage will not break down and retains its granular identity in the sintered microstructure. It appeared likely that if the fines were finely pulverised before returning to the mixing stage the sintered microstructure would not be significantly affected. Unless the fines can be returned in this manner into the processing line, the Cranco would require

removal by a debonding process, involving additional cost.

A test was carried out from the -100 mesh and the -240 mesh fraction of the fines of UO_2-Cranco 253 powder by pressing both into pellets at 20 tons/in^2, debonding in CO_2 and sintering in H_2 at 1600°C. Figures 5 and 6 are the sintered microstructures of the -240 and -100 mesh fractions respectively. The microstructure of Figure 5 is similar to the microstructure of the binder-free powder (Figure 3) while Figure 6 shows segregated porosity resulting from only partial deformation of the powder granules during pressing. The sintered density of the pellets from the -240 mesh fraction was identical to that of the binder-free pellets; from the -100 mesh fraction it was slightly lower. This indicates that reject green pellets containing 10 wt.% of Cranco 253 can be recycled with no significant effect on microstructure or sintered density providing they are pulverised to -240 mesh or finer. The same recycling results would be expected for Cranco 82.

7. SUMMARY AND CONCLUSIONS

On the basis of this work, the most attractive binder was Cranco 253 which when added by wet mixing to a UO_2 powder of comparatively poor pressing characteristics allowed the pressing of pellets at a low reject rate, and their sintering to dense, crack-free pellets with acceptable microstructure. Cranco 253 can be debonded in dry CO_2 for 4 hours at 970°C; treatment in moist N_2-3 Vol.%H_2 was unsatisfactory.

Other binders such as PVA, zinc stearate and Sterotex show some promise and further optimisation of their level and method of addition, and of the debonding and sintering procedure, could give satisfactory results. However, since the main aim of the present work was to select an attractive binder as an alternative to the binder-free route, further optimisation of these binders which were initially unsatisfactory in some respects was not considered justified.

No attempt was made to cost the organic binder and binder-free routes by comparing the overall reject rates and the stages in each route; such an assessment would be meaningful only by comparison on a large scale and using a powder more suitable for pressing without a binder than the powders used in this study. The decision for using an organic binder or binder-free route for large scale production is dependent on many criteria including variations in the powder, the degree of automation in the plant, and the plant size. Such a decision, however, is outside the scope of this report.

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TABLE 1

PROPERTIES OF ELDORADO CERAMIC GRADE UO_2 POWDER

O/U Ratio	Surface Area (m^2/g)	Granulated Powder 10,000 lb/in^2, - 20 + 100 mesh		Green Density* 20 $tons/in^2$ (g/cm^3)	Sintered Density at 1500°C (g/cm^3)	Sintered Defects
		Pour Density (g/cm^3)	Tap Density (g/cm^3)			
2.24	6.6	2.30	2.67	5.4	10.60	Slight Cracking

*Steel die, 0.700 in. dia. bore with exit tapered for 1 in. to 0.009 in. above the bore diameter.

TABLE 2

BINDERS SELECTED FOR EVALUATION IN STAGE I

Binder or Additive	Method of Adding	Addition wt.%
Water	Semi-dry blending	1, 2 and 3
Polyvinyl Alcohol	Dry blending	0.5 and 1.0
Paraffin Wax (as 20 wt.% CCl_4 solution)	Wet mixing	2.0
Carbowax* (as 20 wt.% aqueous solution)	Wet mixing	2.0
Sterotex** (as 5 wt.% CCl_4 solution)	Wet mixing	0.2, 1 and 2
Zinc Stearate	Dry blending	0.2

* Polyethylene glycol. Product of Union Carbide Corporation

** Powdered vegetable oil product manufactured by The Capital City Products Co., U.S.A.

TABLE 3

SUMMARY OF ADDITIVE STUDIES IN STAGE I

Additive and Wt.% Addition		Pour Density (g/cm^3)	Tap Density (g/cm^3)	Flow Rate (sec)	Green Densities (g/cm^3)			Compressive Strength (lb/in^2)		
Water	1	2.08	2.60	55	4.77	5.27	5.42	1100	1220	1210
	2	2.14	2.61	51	4.88	5.25	5.51	990	1430	1430
	3	2.12	2.56	54	4.83	5.28	5.50	1100	1210	1100
PVA	0.5	2.12	2.40	50	4.61	5.16	5.45	990	1110	1210
	1	2.07	2.31	49	4.54	5.03	5.34	1100	1210	1320
Paraffin Wax	2	2.19	2.44	50	4.79	5.25	5.54	1320	1320	1320
Carbowax	2	2.28	2.65	50	4.90	5.37	5.55	1200	1400	1600
Zn Stearate	0.2	2.08	2.33	50	4.65	5.18	5.47	990	1100	1210
Sterotex	0.2	2.08	2.54	50	4.71	5.11	5.38	900	1000	1200
	1	2.2	2.71	51	4.86	5.26	5.53	660	1100	1100
	2	2.16	2.56	49	4.84	5.28	5.57	550	880	990
No additive		2.30	2.67	53	4.80	5.25	5.40	1100	1200	1220
Pressing Pressure ($tons/in^2$)					10	15	20	10	15	20

Pour and Tap Densities and Flow Rate are given for powder precompacted at 10,000 lb/in^2 and granulated to -20 +100 mesh

TABLE 4

SUMMARY OF ADDITIVE STUDIES IN STAGE I

Additive and Wt.% Addition		Sintered Densities (1500°C) (g/cm³)			Average Centre Diameter (inches)			Hourglass Taper (0.001 in.)			Sintered Defects for Pellets Pressed at 20 tons/in²	Impurity Expected and Level Found	Microstructure (20 tons/in²)
Water	1	10.40	10.44	10.40	0.544	0.558	0.565	8	7	6	Badly cracked	C (Nil)	Areas of segregated porosity considered average for this powder. Similar to NA**
	2	9.92	10.37	10.38	0.544	0.558	0.566	8	7	7	Badly cracked	C (Nil)	Similar to NA
	3	10.41	10.40	10.46	0.542	0.558	0.566	10	8	6	Badly cracked	C (Nil)	Similar to NA
PVA	0.5	10.45	10.55	10.58	0.540	0.559	0.570	8	7	7	Slight cracking	C (Nil)	Holes due to binder burnout
	1	10.47	10.50	10.57	0.540	0.557	0.568	11	7	7	Not cracked	C (Nil)	
Paraffin Wax	2	10.00	10.10	10.20	0.545	0.565	0.575	10	8	8	Badly cracked		Similar to NA
Carbowax	2	10.50	10.54	10.54	0.539	0.556	0.565	15	11	10	Badly cracked, end capped		Similar to NA
Zn Stearate	0.2	10.45	10.55	10.58	0.540	0.560	0.569	7	5	6	Not cracked	Zn (5 ppm)	Holes due to binder burnout
Sterotex	0.2	10.47	10.55	10.58	0.537	0.550	-*	10	-*	-*	Slightly cracked	C (Nil)	Similar to NA
	1	10.40	10.45	10.55	0.543	0.558	0.567	10	9	7	Badly cracked	C (Nil)	Similar to NA
	2	10.40	10.45	10.59	0.542	0.556	-*	8	-*	-*	Badly cracked	C (Nil)	Similar to NA
No additive		10.40	10.45	10.57	0.544	0.558	0.566	8	7	6	Slight cracking	C (Nil)	Areas of segregated porosity considered average for this powder
Pressing Pressure (tons/in²)		10	15	20	10	15	20	10	15	20			

* Accurate measurement not possible due to location of crack

** NA = No Additive

TABLE 5

BINDER ADDITIONS IN STAGE II

Binder	Wt.% Added	Method of Addition
PVA (as a 10 wt.% aqueous solution)	1 3 10	Wet mixing
*Cranco 82 (as a 10 wt.% acetone solution)	2 5 10	Wet mixing
*Cranco 253 (as a 10 wt.% acetone solution)	2 5 10	Wet mixing

*Poly-butylmethacrylate in di-butyl phthalate; a product of Imperial Chemical Industries Ltd.

TABLE 6

ABRASION TEST RESULTS FOR GREEN PELLETS WITH VARIOUS BINDER ADDITIONS

Binder	Green Density g/cm^3 (at 20 tons/in^2)	% Weight Lost		
		Test 1	Test 2	Test 3
No addition	5.45	0.39	0.31	Powdered
1 wt.% PVA	5.47	0.12	0.19	2.9
3 wt.% PVA	5.42	0.04	0.06	0.8
10 wt.% PVA	5.01	0.00	0.02	0.3
2 wt.% Cranco 253	5.46	0.55	0.38	Powdered
5 wt.% Cranco 253	5.49	0.25	0.28	8.7
10 wt.% Cranco 253	5.52	0.06	0.12	3.3
2 wt.% Cranco 82	5.47	0.89	0.34	Powdered
5 wt.% Cranco 82	5.57	0.15	0.19	6.2
10 wt.% Cranco 82	5.56	0.06	0.11	2.4

TABLE 7

WEIGHT LOSSES AND SINTERED DENSITIES OF PELLETS

CONTAINING PVA AND CRANCO ADDITIVES

Powder	Debonded in CO_2			Not Debonded	Sintered Density (g/cm^3)		Condition of Sintered Pellets		Hourglass Taper (inches)
	% Weight Loss Due to Debonding (800°C)	% Weight Loss Sintering (1600°C)	Carbon Level (ppm)	% Weight Loss in Sintering	Debonded	Not Debonded	Debonded	Not Debonded	Debonded
No addition	0.38	0.54	< 5	0.91	10.55	10.53	Not cracked	Not cracked	0.004
1 wt.% PVA	1.31	0.61	< 5	2.0	10.51	10.2	Not cracked	Not cracked	0.007
3 wt.% PVA	3.1	0.7	< 5	3.9	10.4	9.8	Cracked	Badly cracked	0.009
10 wt.% PVA	8.9	1.14	< 5	10.0	Approx.10	Porous badly cracked	Cracked	Badly cracked	0.009
2 wt.% Cranco 253	1.1	0.55	< 5	1.63	10.53	10.53	Not cracked	Not cracked	0.003
5 wt.% Cranco 253	2.06	0.52	< 5	2.57	10.51	10.4	Not cracked	Not cracked	0.003
10 wt.% Cranco 253	3.7	0.516	< 5	4.21	10.40	10.2	Not cracked	Not cracked	0.003
2 wt.% Cranco 82	1.11	0.50	< 5	1.60	10.54	10.53	Not cracked	Not cracked	0.003
5 wt.% Cranco 82	2.28	0.52	< 5	2.78	10.53	10.3	Not cracked	Not cracked	0.003
10 wt.% Cranco 82	3.85	0.53	< 5	4.37	10.53	9.9	Not cracked	Not cracked	0.003

TABLE 8

EFFECT OF HEATING CRANCO AND PVA IN CO_2 AND MOIST N_2-3 VOL.%H_2

Temperature °C	Dry Powdered Cranco 82		PVA	
	CO_2	Moist N_2-3 Vol.%H_2	CO_2	Moist N_2-3 Vol.%H_2
EXPERIMENT A				
100	Liquified	as for CO_2		
250			Swelling	as for CO_2
300	Commenced to vaporise	as for CO_2		
400	White fumes, yellow condensate, carbonaceous deposit	as for CO_2		
450			Carbonised	as for CO_2
500-600	No change	as for CO_2		
650			No change	as for CO_2
800	Deposit removed	Deposit still present	Greater part of deposit removed	No apparent removal of deposit
850				
EXPERIMENT B				
700	Deposit almost removed	Large amount of deposit remaining	Greater part of deposit removed	No apparent removal of deposit

TABLE 9

ABRASION TESTS IN STAGE III

Binder Added	Percentage Weight Loss		
	Test 1	Test 2	Test 3
3 wt.% PVA	0.05	0.05	1.62
5 wt.% PVA	0.05	0.04	1.11
10 wt.% Cranco 253	0.03	0.04	1.37
15 wt.% " 253	0.01	0.01	0.58
10 wt.% " 82	0.15	0.03	1.21
15 wt.% " 82	0.01	0.02	0.50
No addition	1.5	0.19	Powdered

TABLE 10

EFFECTS OF BINDER ADDITIONS TO UO_2 WHEN PELLETS ARE DEBONDED IN MOIST N_2-3 VOL.%H_2

Binder Addition	Green Density at 20 tons/in^2 (g/cm^3)	Sintered Density at 1600°C (g/cm^3)		Sintered Defects
		Debonded 850°C	Debonded 975°C	
3 wt.% PVA	5.48	-*	-*	Badly cracked at both debonding temperatures
5 wt.% PVA	5.31	-*	-*	Badly cracked at both debonding temperatures
10 wt.% Cranco 253	5.53	10.26	-	Slight cracking and some distortion
15 wt.% Cranco 253	5.28	-	-	-
10 wt.% Cranco 82	5.74	10.3	-*	Slight cracking, some distortion, more pronounced with 975°C debonding
15 wt.% Cranco 253	5.65	10.0	-*	Slight cracking and no distortion at 850°C. Cracking worse with 975°C debonding
No addition	5.58	10.53	-*	Slight cracking at 850°C; bad cracking at 975°C

-* Pellets too badly cracked for density determination

- No pellet in test

TABLE 11

EFFECTS OF BINDER ADDITIONS TO UO_2 SINTERED IN MOIST N_2-3 VOL.%H_2 WITHOUT SEPARATE DEBONDING

Binder Addition	Sintered Density (1400°C - 2 hrs) (g/cm)	Sintered Defects
3 wt.% PVA	~ 9.7	Severe cracking and distortion
5 wt.% PVA	~ 9.8	" " " "
10 wt.% Cranco 253	10.05	Slight cracking
15 wt.% Cranco 253	10.01	" "
10 wt.% Cranco 82	10.01	" "
15 wt.% Cranco 82	10.02	" "
No addition	10.61	" "

TABLE 12

ESTIMATED PERCENTAGE OF UNREMOVED BINDER AFTER DEBONDING IN MOIST N_2-3 VOL.%H_2

Debonding Temperature ^{o}C	Flow Rate cm^3/min	Estimated % of Unremoved Binder				
		3 wt.% PVA	5 wt.% PVA	10 wt.% Cranco 253	10 wt.% Cranco 82	15 wt.% Cranco 82
850	200	0.8	1.4	0.1	0.1	Nil
975	200	0.6	1.1	Nil	0.1	Nil
975	250	0.4	1.1	Nil	Nil	Nil

Note: No estimate was made for 15 wt.% Cranco 253

TABLE 13

EFFECTS OF PVA AND CRANCO BINDER ADDITIONS ON UO_2 WHEN DEBONDED IN CO_2

Binder Addition	Green Density (g/cm^3)	Sintered Density 1600°C (g/cm^3)					
		Debonded 600°C	Debonded 800°C		Debonded 850°C	Debonded 975°C	
		Normal Flow	Normal Flow	Fast Flow	Normal Flow	Normal Flow	Fast Flow
3 wt.% PVA	5.48	**	**	**	**	**	** 10.42
5 wt.% PVA	5.31	**	**	**	**	**	** 10.36
10 wt.% Cranco 253	5.53	* 10.26	10.63	* 10.64	10.66	* 10.62	10.65
15 wt.% Cranco 253	5.28	* 9.8	10.66	10.66	* 10.65	*	10.64
10 wt.% Cranco 82	5.74	* 10.6	* 10.67	10.63	* 10.68	* 10.64	10.65
15 wt.% Cranco 82	5.65	*	10.66	10.66	10.66	* 10.64	10.65
No Addition	5.58	* 10.61	* 10.63	* 10.63	* 10.63	* 10.62	10.62

Normal Flow 200 cm^3/min Fast Flow 250 cm^3/min

Where not mentioned, no cracks

* Fine cracking

** Bad cracking

TABLE 14

ESTIMATED PERCENTAGE OF UNREMOVED BINDER AFTER DEBONDING IN CO_2

Debonding Temperature °C	Flow Rate (cm^3/min)	Estimated % of Unremoved Binder					
		3 wt.% PVA	5 wt.% PVA	10 wt.% Cranco 253	15 wt.% Cranco 253	10 wt.% Cranco 82	15 wt.% Cranco 82
600	200	1.1	1.2	Nil	0.1	Nil	0.1
800	200	0.3	0.5	Nil	Nil	Nil	Nil
800	250	Nil	0.7	Nil	Nil	Nil	Nil
850	200	0.1	0.2	0.1	Nil	Nil	Nil
975	150	0.6	0.8	Nil	Nil	Nil	Nil
975	200	Nil	0.3	Nil	Nil	Nil	Nil

TABLE 15

POUR, TAP AND GREEN DENSITIES OF UO_2 WITH AND WITHOUT CRANCO BINDER ADDITIONS

Powder	Granulated to -22 mesh		Green Densities Pressed at 20 tons/in^2 (g/cm^3)	
	Pour Density (g/cm^3)	Tap Density (g/cm^3)	Die Lubricated	Die Not Lubricated
10 wt.% Cranco 253	2.0	2.26	5.73	5.66
10 wt.% Cranco 82	2.35	2.57	5.69	5.65
No additive	2.43	2.79	5.47	-

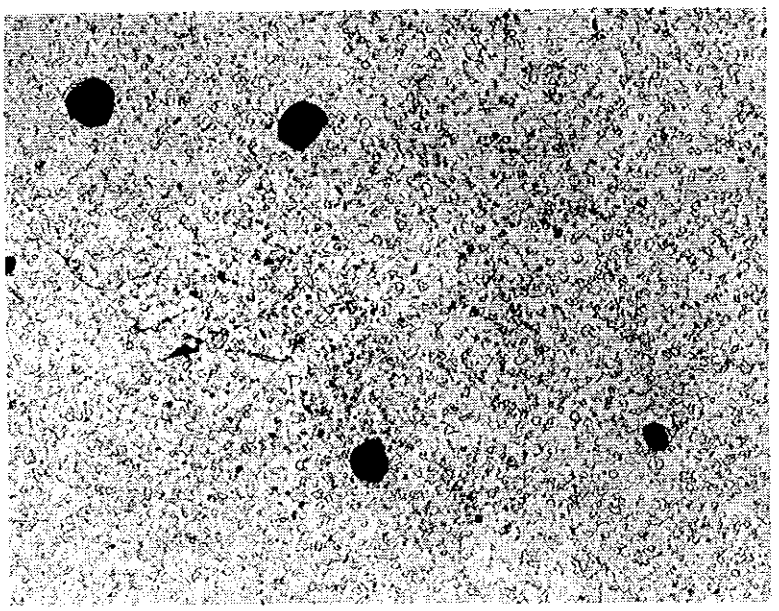
TABLE 16

SUMMARY OF SINTERING RESULTS FROM STAGE IV

Powder	Tray Number	Number of Pellets on Tray	Number Cracked	Number Chipped	Percentage with Visible Cracking	Final Total Percentage of Rejects Due to Cracking	Mean Sintered Density (g/cm^3)	Hourglass Taper (inches)	
								Die Not Lubricated	Die Lubricated
Cranco 253	1	20	Nil	Nil	Nil	2	10.64	0.004	0.002
	2	20	Nil	Nil	Nil		10.66		
	3	16	4	Nil	25*		10.66		
Cranco 82	4	20	6	Nil	30*	10	10.66	0.005	0.003
	5	20	7	Nil	35*		10.65		
	6	16	12	Nil	75*		10.67		
	7	8	6	Nil	75*		10.66		
No Additive	9	23	10	23	44**	50	10.66	0.005	
	10	23	13	23	56**		10.67		

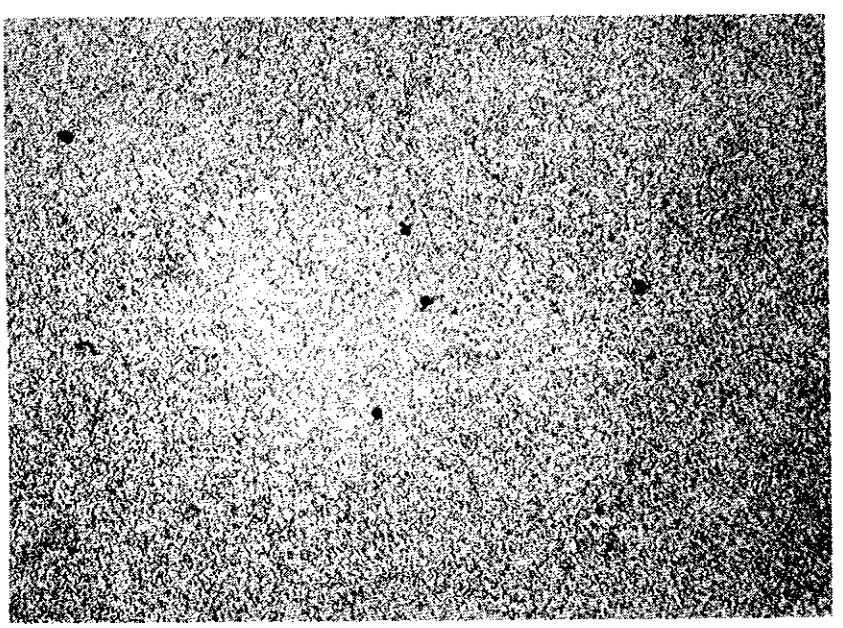
* Mainly fine surface cracks, removed in centreless grinding

** Large open cracks



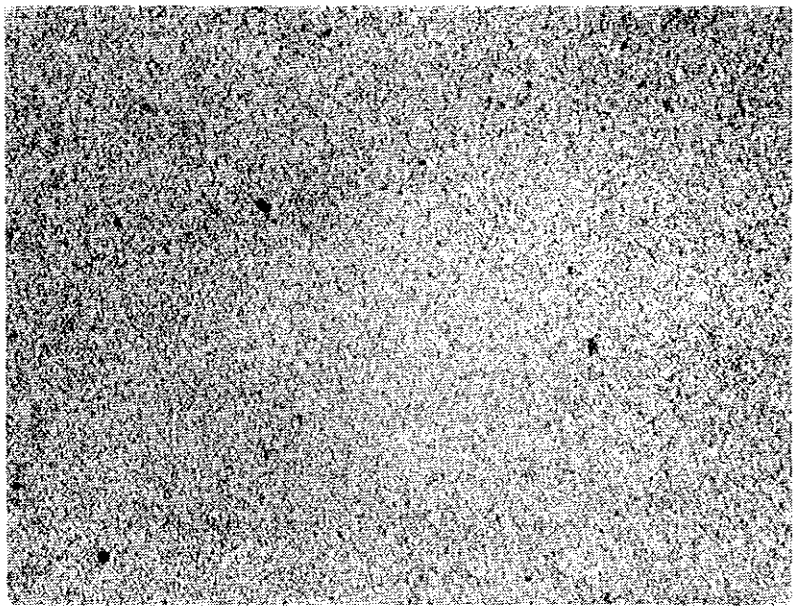
(X 100)

FIGURE 1. BURNOUT POROSITY IN SINTERED UO_2 RESULTING FROM THE ADDITION OF DRY POWDERED ZINC STEARATE



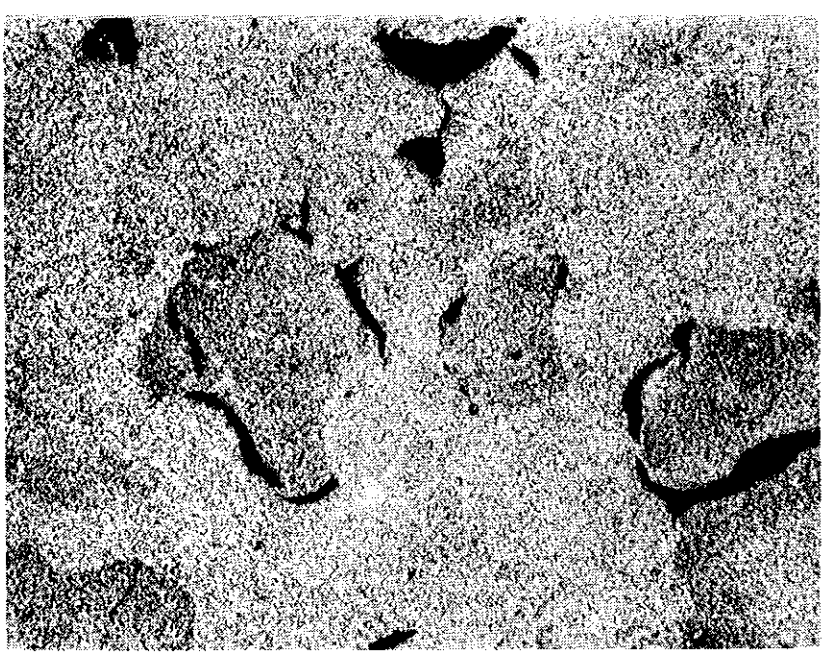
(X 50)

FIGURE 2. MICROSTRUCTURE OF SINTERED UO_2 RESULTING FROM 15 wt.% CRANCO BINDER ADDITION



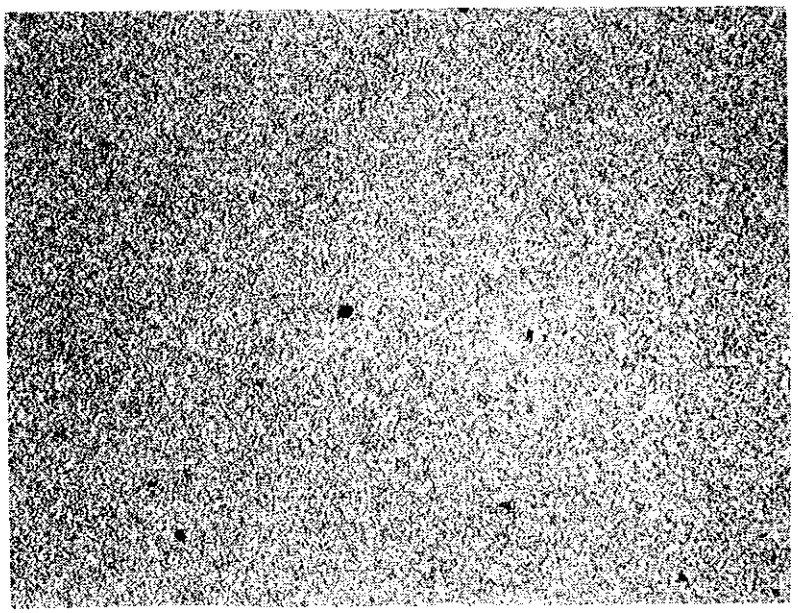
(X 50)

FIGURE 3. MICROSTRUCTURE OF SINTERED UO_2 WITH NO BINDER ADDITION



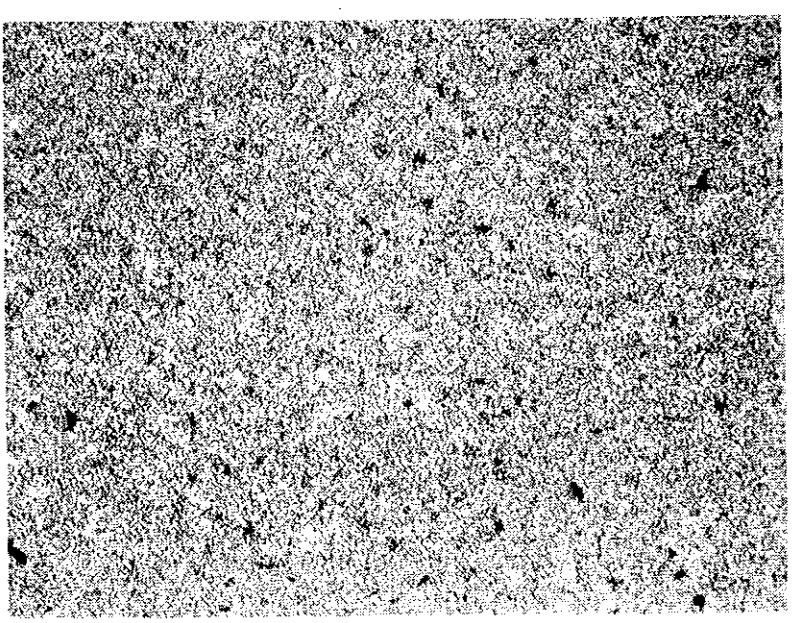
(X 50)

FIGURE 4. MICROSTRUCTURE OF SINTERED UO_2 RESULTING FROM 5 wt.% PVA ADDITION



(X 50)

FIGURE 5. MICROSTRUCTURE OF SINTERED UO_2
PRESSED FROM -240 MESH FINES
CONTAINING 10 wt.% CRANCO 253



(X 50)

FIGURE 6. MICROSTRUCTURE OF SINTERED UO_2
PRESSED FROM -100 MESH FINES
CONTAINING 10 wt.% CRANCO 253