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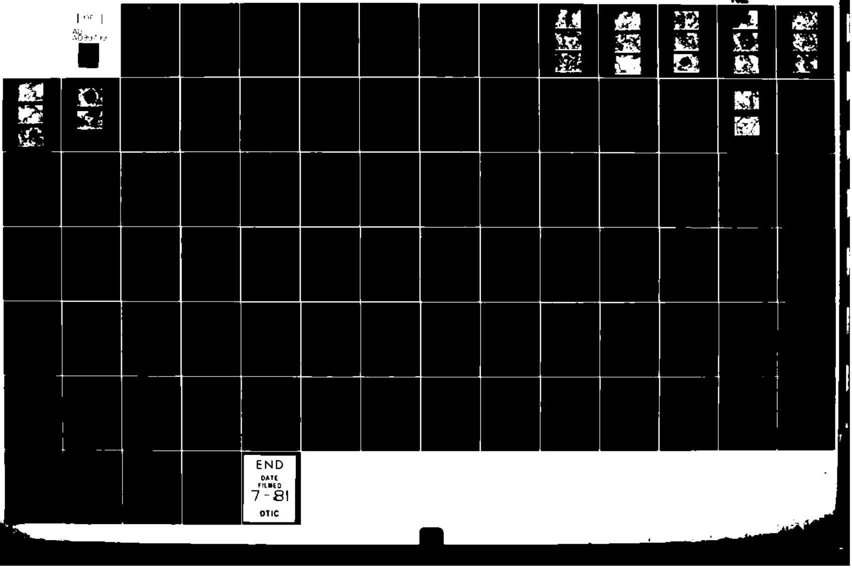

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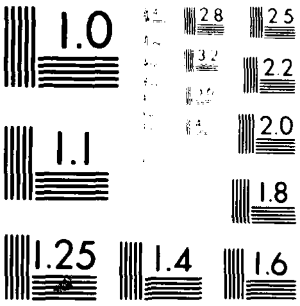

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Extensive studies of the effects of various sintering parameters and many substituents on the mechanical properties of tungsten test samples produced by powder metallurgical methods have been completed. As final result of this work it can be stated that the influence of the sintering parameters is much more pronounced than that of the purity of the starting W powders, if they are in the normal range of a good high quality industrial product. For both absolute values and reproducibility of →

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Final Technical Report

The influence of chemistry and various fabrication parameters on the properties of tungsten heavy metals

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TU Vienna

Vienna, Feb.1981

INTRODUCTION

The final aim of this two years' project was the improvement of tungsten heavy metals, especially with regard to two of their mechanical properties, of which tensile strength and elongation were the most important.

The improvements were to be achieved by investigating the influence of the production parameters, esp. sintering cycle and sintering parameters, and the effect of impurities, both in the starting W-powders and the binder phase, on the mechanical properties of the sintered samples. To recognize even slight effects with certainty, the sintering had to be performed exactly according to the pre-set sintering cycle, so that an excellent reproducibility of the results could be achieved.

During the first year's work on this project, the investigations concentrated mainly on the fabrication parameters of heavy metals with sufficiently good mechanical properties. The influence of grain size and grain size distribution of the W-powders as well as the effect of different pressing lubricants on the compactibility of the powder mixtures were thoroughly examined. It was found that powders with a grain size of ~3 µm give the best results; after addition of 1% camphor and a granulation treatment, the powders can be compacted without difficulty at pressures up to 5 t/cm^2.

Early sintering experiments showed that a minimum temperature of 1460°C is necessary for the production of nonporous samples; higher W-contents (95 and 97%W) require a somewhat higher sintering temperature. A sintering time of 30 min was found to be optimal for all compositions; unwelcome grain coarsening could thus be avoided.

The sintering tests also showed the decisive importance of a thorough pre-reduction treatment of the samples before sintering. Poor de-oxidation resulted in extremely low ductility and causes a decrease and a wide scatter in tensile strength values. With a uniform composition of 90 wt% W, 6,7 wt% Ni, 3,3 wt% Fe, carefully pre-reduced samples showed tensile strengths of up to 1000 N/mm^2 and elongations of up to 27% with surprisingly good reproducibility; even with heavy metals containing 95% W, elongation values of 13% could be obtained. The addition of reducing metals to the binder as Cr and V, did not render the pre-reduction unnecessary; the elongations thus achieved were only half those of pre-reduction samples.

After a sintering cycle had been found that resulted in good mechanical properties obtainable with a very high rate of reproducibility, further investigations into production parameters and also into the influence of impurities became possible during the second year. Of the many possible directions of research, the most promising were:

1) Simplification of the sintering cycle:
   The sintering cycle most effective in our experiments is not easily reproducible in industrial furnaces; a sintering cycle consisting of several stages at fixed temperatures could be controlled more easily. Optimization of the duration and temperature of these steps, therefore, was regarded as a main target for the investigations.

2) Sintering and heat treatments in various atmospheres:
Several authors claim that heat treatment of the sintered heavy metals in hydrogen (1) or under vacuum (2,3) is essential for the production of W heavy metals with high tensile strength and elongation. Our experiments (see First Annual Report) had shown that samples cooled slowly from sintering temperature to 500°C had almost twice the elongation of rapidly cooled samples. It was to be investigated if this discrepancy was caused by the sintering atmosphere or if it was an effect inherent in the system W-Ni-Fe.

3) Addition of small amounts of other metals to the Ni-Fe-binder:
In the literature, many metals have been used as additives to W heavy metals. These additives were usually in the range of several wt% of the mixture and often comprised metals whose prices were, of have now become rather high (e.g. Co). It seemed promising, therefore, to reduce the content of those metals, without greatly reducing the desirable effects.

4) Investigations into the influence of trace impurities contained in the starting W powders:
As there are many types of W powders, which, due to their different origins, contain different amounts of impurities, knowledge about positive or negative influences of impurities would be helpful in the selection of W-powders for the production of W heavy metals. Further definitely positive influences of certain impurities might recommend the doping of the W powders with these elements.

Summary of the experimental work performed:

1) Description of the starting materials:

The W powders used in the experiments were specially prepared for us and supplied by local tungsten manufacturer. Requested powders with various doping additives were produced. Tab.1 shows the specifications of the powders regarding chemical purity and mean grain size as determined by Fisher SSS; these results are in good agreement with the grain size distribution spectra determined by standard sedimentation methods (see appendix); these data were supplied by the manufacturer together with the powders. Normally the average grain size is near 3 μm, although a few powders are considerably coarser, up to ~10 μm. These powders have a somewhat broader grain size distribution spectra than the finer ones. Chemically, the W-powders are very pure. Except for the doping additives, the impurities are in the range of <20 ppm, with several elements <10 ppm. From the difference between the amount of doping elements added before reduction of the WO_3 and the analyses after reduction it is evident that some elements, e.g. Na, evaporate to a very large extent during reduction. This behavior has also been reported by Lassner et al.(4).

SEM-photos(Fig.1-20) clearly show the quite similar appearance of the different W powders. There are some differences in their tencency to form agglomerates, and some powders exhibit more pronounced crystal facets on the particles than others. However, only the powder E 14W containing Al is markedly different from the other ones, the surface of the grains being covered with small rods and dots. Analyses have shown, that these contaminations consists mainly of Al_2O_3.

Table 1: Chemical Analysis of the W-powder (contents in ppm)

	Additive	C	O_2	P	Al	Ca	Co	Cr	Cu	Fe	K	Mg	Mo	Na	Ni	Si	V
503		20	240	21	< 10	< 10				12			< 20	26	< 10	< 20	
E 2	250 Na	7	130	42	< 10	< 10				< 10			< 20	20	< 10	< 20	
E 5	250 Li	4	630	44	< 10	< 10				< 10			< 20	< 10	< 10	< 20	
E 8	188 Ca	15	280	43	< 10	220				< 10			< 20	< 10	< 10	< 20	
E 11	250 B	24	760	48	< 10	< 10				< 10			< 20	22	< 10	< 20	
E 14	250 Al	17	470	37	288	< 10				< 10			< 20	22	< 10	< 20	
E 17	100 Si	11	470	24	< 10	12	< 10	< 20	< 10	12	14	< 10	< 20	48	< 10	96	< 25
E 21	140 Na, 100 P	24	310	93	< 10	< 10	< 10	< 20	< 10	< 10	< 10	< 10	< 20	24	< 10	< 20	< 25
E 24	100 As, Sb, Bi	15	640	31	< 10	12	< 10	< 20	< 10	24	< 10	< 10	< 20	26	12	< 20	< 25
E 27	100 U	11	450	29	< 10	16	< 10	< 20	< 10	< 10	< 10	< 10	< 20	18	< 10	< 20	< 25
E 30	188 Na, 106 Al 113 U, 500 F	14	220	52	64	< 10				12			< 20	48	< 10	< 20	
E 33		11	310	49	< 10	< 10				< 10			< 20	14	< 10	< 20	
E 36	100 Na	13	240	30	< 10	12	< 10	< 20	< 10	< 10	14	< 10	< 20	22	< 10	< 20	< 25
E 39	50 Na	6	270	23	< 10	16	< 10	< 20	< 10	< 10	10	< 10	< 20	22	< 10	< 20	< 25
E 45	100 Li	4	530	36	< 10	< 10	< 10	< 20	< 10	< 10	< 10	< 10	< 20	< 10	< 10	< 20	

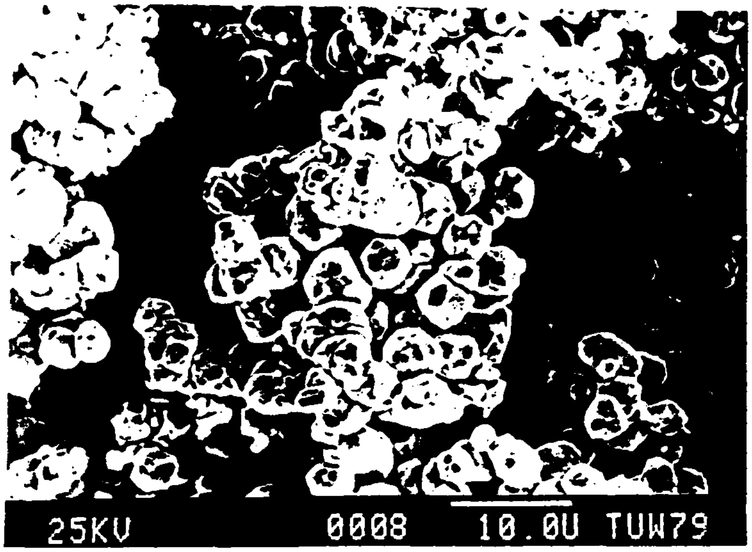


Fig.1
E2W

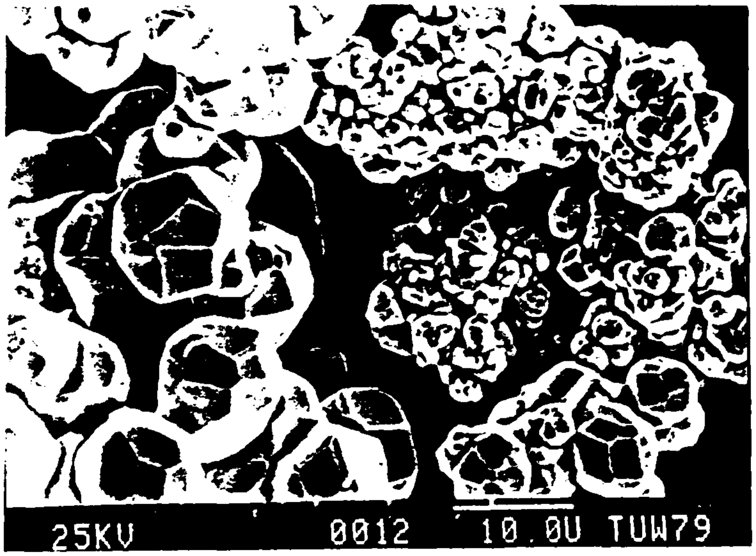


Fig.2
E5W

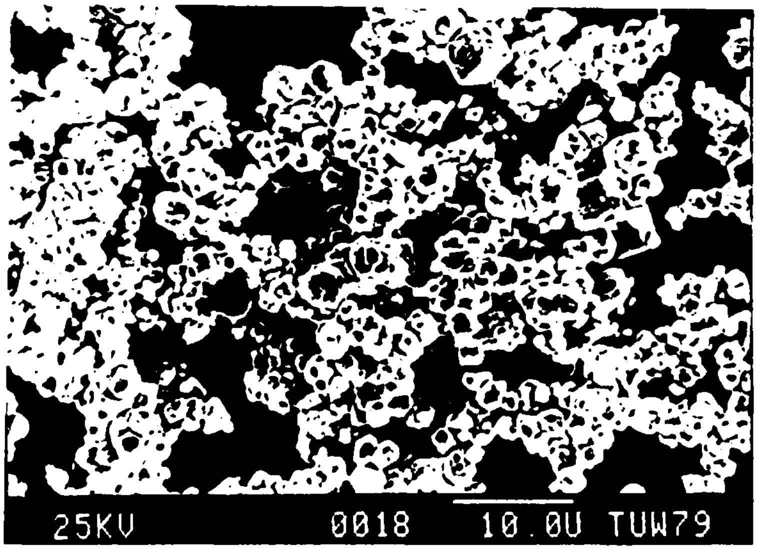


Fig.3
E8W

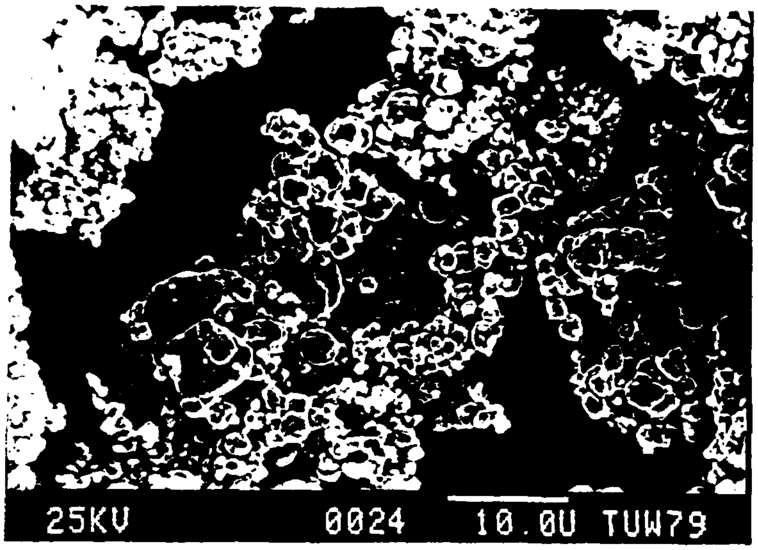


Fig.4
E11W

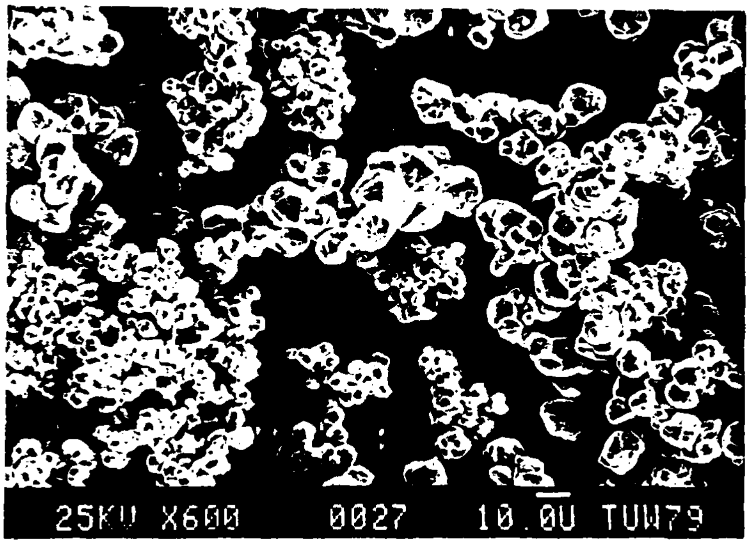


Fig.5
E14W

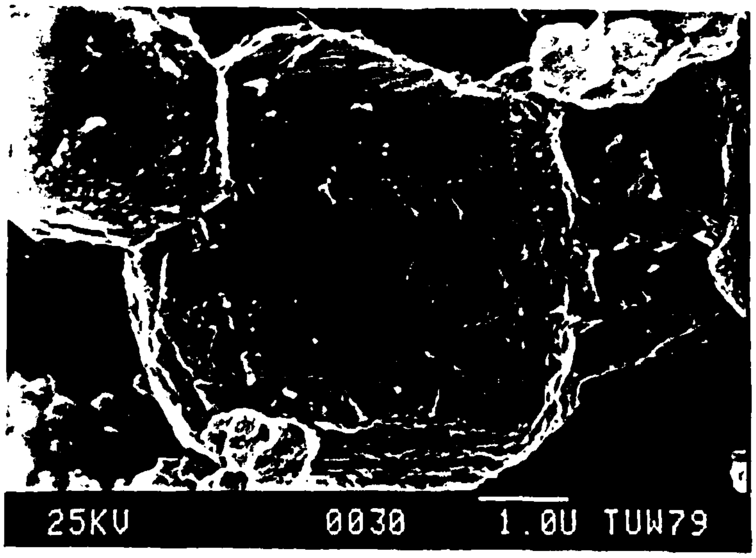


Fig.6
E14W

Fig.7
E17W

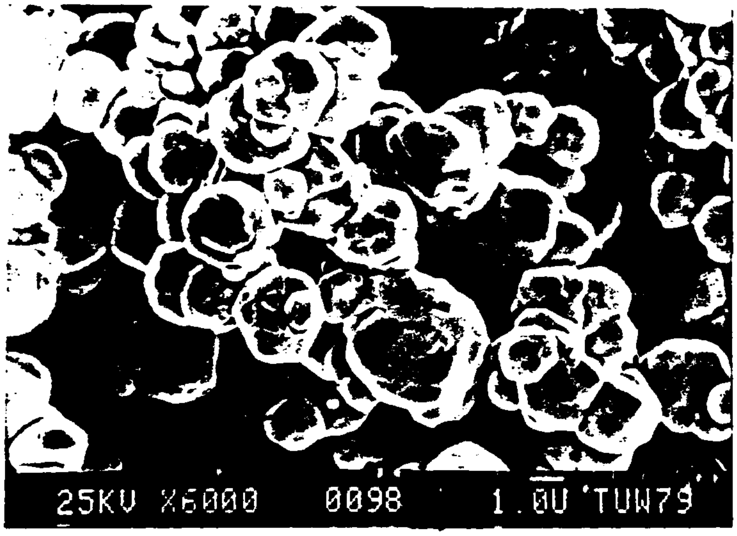


Fig.8
E21W

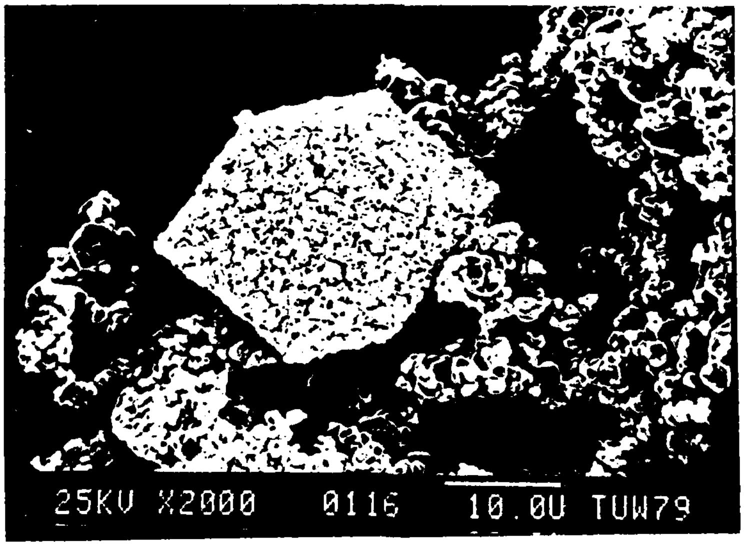


Fig.9
E24W

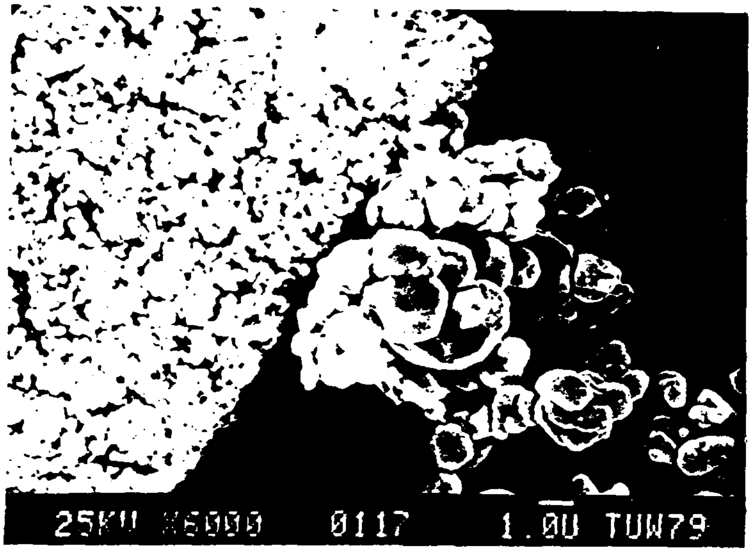


Fig.10
E24

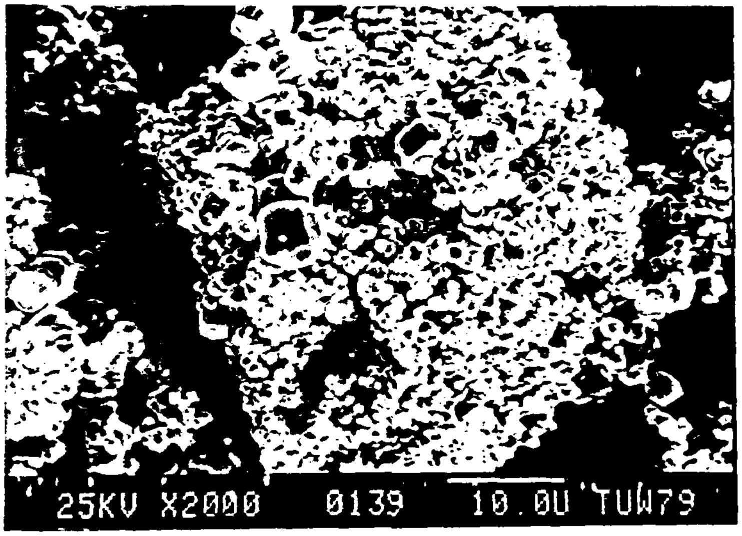


Fig.11
E27

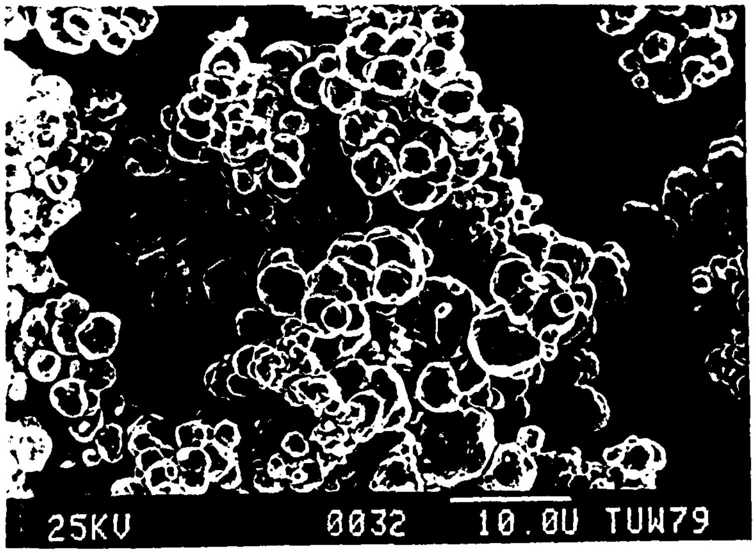


Fig.12
E30

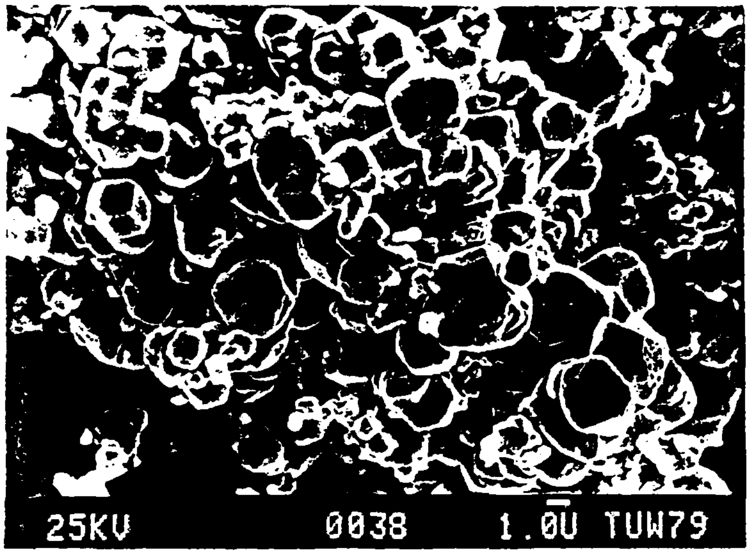


Fig.13
E33W

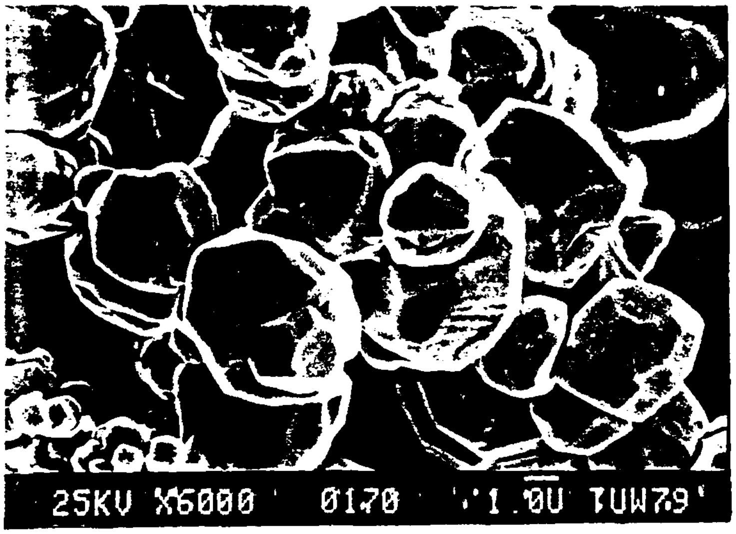


Fig.14
E36W

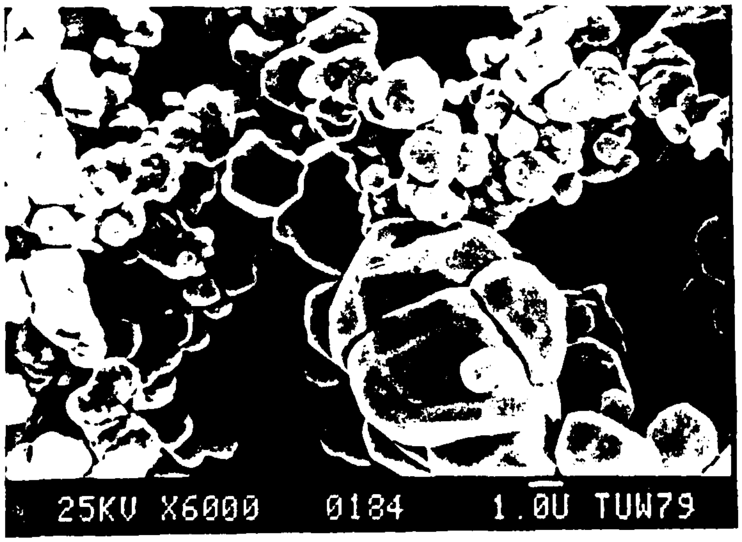


Fig.15
E39W

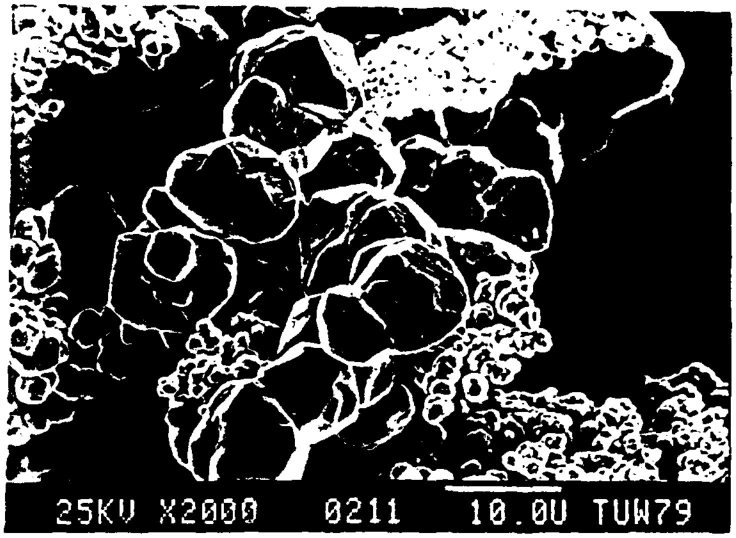


Fig.16
E45W

Fig.17
E45W

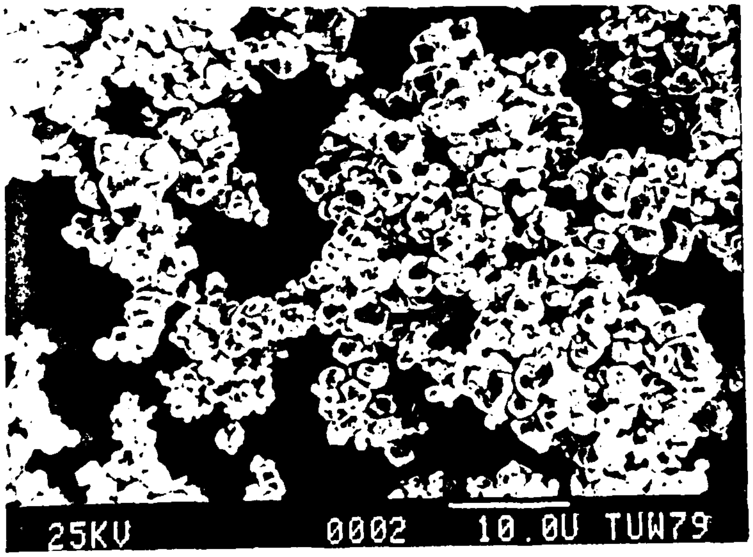


Fig.18
W5O3

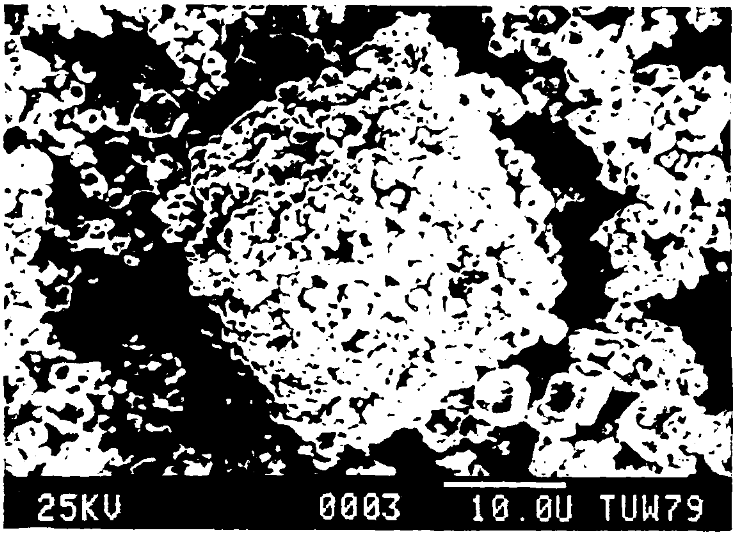


Fig.19
W5O3

Fig.2o
W5O3

The Fe and Ni powders supplied by BASF, Germany, were of carbonyl quality. Their grain sizes were around 5 µm, the C-content was219 ppm for Fe and 707 for Ni, and the O-content was 2020 and 910 ppm respectively. The pressing tests had shown that best results were obtained with 1% camphor as a pressing aid; all further experiments were carried out with this amount of pressing lubricant.

2) Preparation and testing of the samples

The green compacts were prepared as described in our previous reports; the powder mixtures, always consisting of 90 wt% W, 6.7 wt% Ni, 3.3 wt% Fe, were wet mixed in cyclohexane with 1% camphor as pressing lubricant. After 3 hrs of mixing in a rotation mixer the cyclohexane was partially evaporated; the still damp powder was then granulated through a 0,8 mm mesh sieve and afterwards dried thoroughly.

The powders were compacted to standard tensile strength bars 1 sq.in. in area (MPIF Standard 10-63) in a pressing tool with floating die to ensure uniform pressure from above and below. Pressure was applied by means of a 150 ton capacity hydraulic press. For the compaction of the W-Ni-Fe-powder mixtures, a pressure 5,15 tons/cm^2 was found to be optimal for giving sufficient densities without causing pressing faults.

The green samples were sintered in a furnace with a Mo heat conducting coil for temperatures up to 1650°C. The furnace always was operated in a reducing atmosphere, usually H_2 of technical purity. The temperature regulation allowed the furnace to be maintained within ±5°C of the set temperature. This exactness was essential for obtaining the necessary reproducibility.

The samples were transported in Mo boats, usually 8 bars per boat. To prevent them from fusing together during sintering, the space between them was filled with Al_2O_3 powder. The front ends of the bars were usually left uncovered to permit the observation of the "silberblick" effect - the first melting of the liquid phase - when the samples suddenly become darker than the surrounding Al_2O_3. To make it possible to control the furnace temperature by pyrometer and to move the boats inside the furnace without opening the shutter, a special shutter was constructed which incorporated a stuffing box for a long hook and as small bulleye whose glass cover could be removed to avoid false temperature measurements becuuse of the absorption of the radiation by the glass. Thus the intrusion of oxygen into the furnace atmosphere could be kept minimum.

After sintering, the interesting properties of the test bars were measured.To determine the sinter compact density, the water buoyancy method was used, which gives more accurate results than the Hg displacement method.

The hardness was checked on a Vickers tester, with a weight of 62,5 kp. Whenever promising, microhardness values were determined on metallographic sections to check the difference in hardness between grains and binder phase.

A tensile tester with a maximum load of 30 kN was used for the determination of tensile strength and elongations, the gage length being 25 mm.

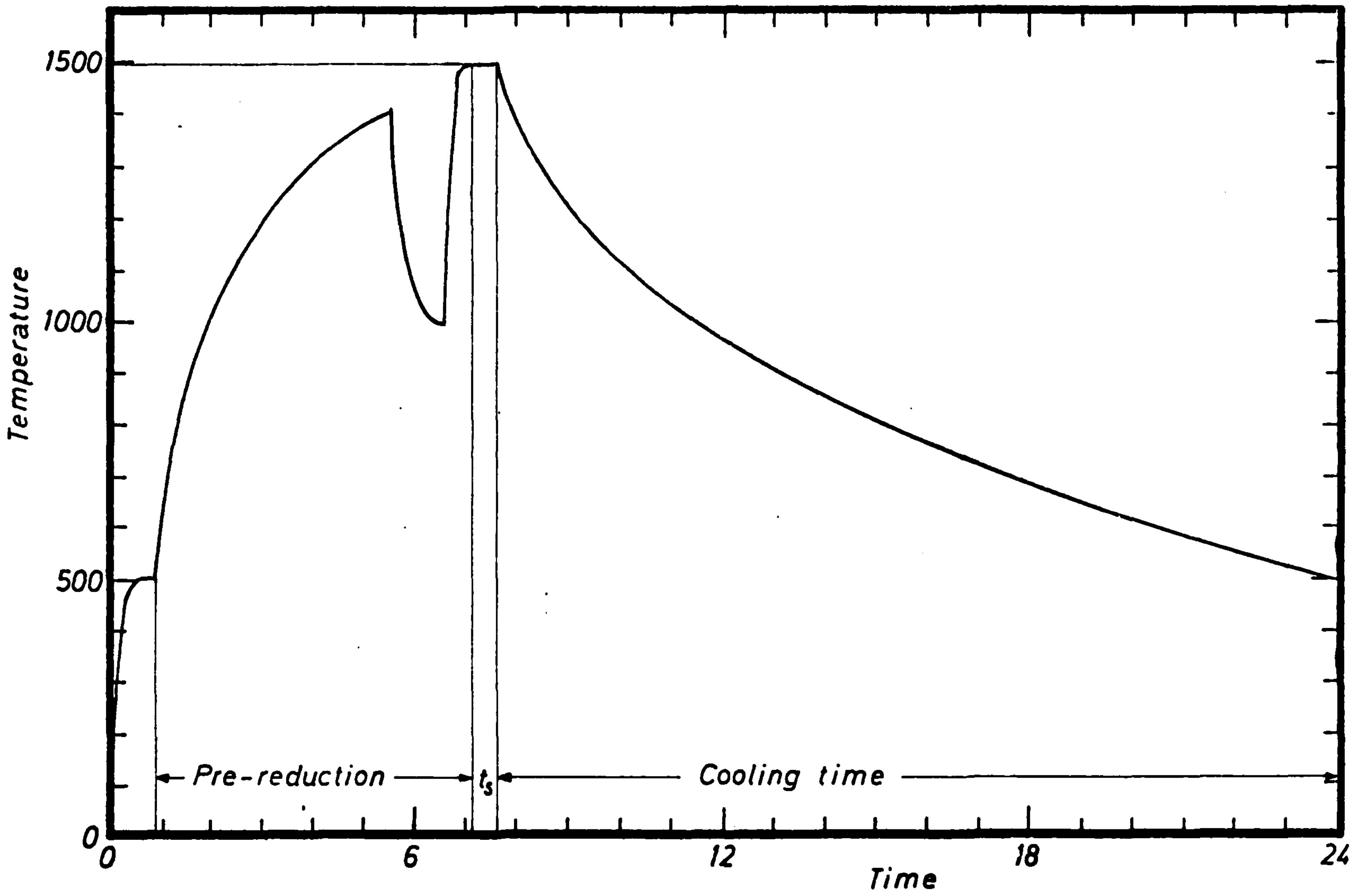


Fig.21: Temperature-time-diagram for the standard sintering cycle

3) Variation and simplification of the sintering cycle:

The sintering cycle found best in our experiments was easily reproducible in our furnace, but was adapted for the special heating and cooling characteristica of this laboratory Mo-furnace. To make our experiments reproducible in industrial furnaces, it was recommendable that a sintering cycle consisting of steps at constant temperature levels especially in case of the pre-reduction, be found. For this purpose, the individual steps of the sintering cycle were evaluated more carefully.

3.1 Removal of the pressing lubricant

Although earlier experiments had shown (see First Annual Report) that embrittlement by carbon did not normally occur in W heavy metals, it seemed possible that, for example, a too rapid heating of the green compacts would lead to decomposition of the camphor thus contaminating the alloy with carbon. To evaluate this possibility, several de-waxing treatments were tried: first of all, a normal de-waxing by shoving the samples into the heating zone of the furnace at 500°C, where they remained for 60 min; then the sintering was carried out as usual (Fig.21). Second, a very slow de-waxing was tried where the samples were pushed stepwise into the furnace, thus requiring 60 min to reach 500°C. The third de-waxing was a shock treatment: the samples were pushed immediately into the 1200°C heating zone. Further treatment and sintering were performed as usual. In this last case comparison samples without any pressing lubricant at all were also sintered together with the usual 1% camphor green samples to determine any detrimental influence of the pressing lubricant (Tab.2).

Table 2: Mechanical properties of samples with different de-waxing treatments (W 503/79); 3 hrs pre-reduction at 1200°C; 1490°C, t_s 30 min; average values from 4 samples.

	Density g/cm^3	σ_B (MPa)	Elongation (%)	Hardness 62.5
slow de-waxing	17,072±0,005	734±14	2,1±0,6	289±4
nomal de-waxing	17,05 ±0,01	930±18	23,0+1,3	293±3
shock de-waxing (1% camphor)	17,051±0,02	1007±12	20,5±2,4	292±2
no lubricant	17,040±0,01	997±10	20,2±2,0	288±1,5

As seen in Tab.2, the most careful de-waxing process resulted in the most brittle products, while the shock de-waxing did not cause any deterioration of the mechanical properties; In this case, samples with and without camphor showed the same elongations after sintering.

Presumably in the slow de-waxing process the lubricant reacts with the metal powder before it has completely evaporated; the resulting layers of WC inhibit the wetting of the W grains by the binder in the following sintering process. In the normal de-waxing and particularly in the shock treatment the pressing lubricant evaporates before a significant reaction is possible.

Formation of pores or cracking did not occur; the green porosity of more than 30% is sufficiently high to permit easy evaporation of the camphor evaporate without obstacles.

It is conceivable, however, that with larger samples difficulties with de-waxing might be encountered; Industrial practice usually compacts heavy metals isostatically without adding pressing lubricant. It might be of interest, too, to produce heavy metals by die compaction without pressing lubricant. To check the behavior and properties of such heavy metal products a series of tests using samples with and without pressing lubricant was carried out. The composition of the mixtures used was the usual 90% W, 6.7% Ni, 3.3% Fe with standard W powder 503/79 (3.05 µm). As could be expected, the compaction of the powder mixtures without pressing lubricant was considerably more difficult; uniform filling of the powder in the die was of decisive importance to avoid pressing faults (Tab.3).

<u>Table 3:</u> Mechanical properties of samples without pressing lubricant. Standard powder W503/79; sintering Cycle 2 (slow heating and cooling). Average value from 4 Samples. In brackets samples with 1% camphor. Green density at 5,15 ton/cm^2: 10,785 g/cm^3 (11,52 g/cm^3)

	Density (g/cm^3)	Hardness 62,5	σ_B (MPa)	δ Elongation (%)
Cycle 2; 1475°C	16,991±0,04 (17,073±0,01)	303±4 (295±4)	838±9 (925±14)	0,55±0,3 (23,7 ±3,2)
Cycle 2; 1490°C	17,062±0,016 (17,046±0,02)	298±3 (293±3)	1005±4 (962±13)	22,6 ±1,4 (24,6 ±1,1)
Cycle 2; 1510°C	17,030±0,02 (17,062±0,16)	293±4 (285±3)	980±8 (923±11)	24,2 ±2,6 (19,7 ±1,2)$^{x)}$

x) strongly rounded edges

Samples without pressing lubricant apparently must be sintered at a considerably higher temperature; densities of ~100% and sufficient tensile strengths and elongation were obtained here at temperatures of 1490°C and 1510°C as compared to 1470°C-1490°C for normal specimens with 1% camphor. The mechanical properties were within the usual range; as the handling of green compacts pressed without camphor requires much care and since no difficulties with lubricant bake out were encountered, it was decided to use pressing lubricant for all further experiments.

[illegible].2. Pre-reduction of the green compacts:

For simplification of the sintering cycle, we decided to carry out pre-reduction of the green compacts as fixed temperatures for a given length of time. Green compacts were de-waxed at 500°C for 60 min, then the furnace was heated up to pre-reduction temperature and the samples were pushed in. After 3 hrs, the samples were pulled into a cooler zone, the furnace were heated up to sintering temperature and the samples were pushed back into the hot zone for sintering. Afterwards the furnace was switched off and the samples remeined there for cooling (cooling rate see Fig. 21).

Table 4: Mechanical properties of heavy metals pre-reduced for 3 hrs at different temperatures. Sintered 30 min at 1470°C, slow cooling (Average values from 4 samples)

Pre-reduction temperature	Density g/cm^3	Hardness Hv 62,5	σ_B MPa	Dehnung %
800	17,111	289	720±19	3,1±1,5
1000	17,122	302	940±21	16,3±2,3
1100	17,109	307	947±16	20,9±1,4
1200	17,102	299	954±9	22,1±0,8
1300	17,122	296	917±6	13,8±1,4
1400	17,091	293	895±24	5,0±3,2

The tests show that temperatures below 1000°C are somewhat too low for satisfactory pre-reduction; probably the reduction rate is not high enough. The optimal pre-reduction temperature seems to be in the range of 1000-1200°C; elongations of >20% can be obtained without difficulties. The very low elongations observed after pre-reduction temperatures of 1300°C or more can be explained by the fact that at temperatures relatively close to the melting point of the liquid phase the solid phase sintering proceeds so fast that the pores close up before complete de-oxidation can occur. Samples pre-reduced for 3 hrs at 1300°C and taken out of the furnace had shrunk almost to the size of liquid phase sintered samples.

Further support for this explanation comes from the fact that samples pre-reduced at 1000-1200°C pulled afterwards into the water-cooled zone of the furnace and then sintered resulted in very low elongations, while samples pre-reduced, by heating them slowly from 500 to 1400°C (Fig. 21) suffered no damage by this intermediate cooling. In this case the reverse effect occured: during the cooling process the water vapor present in the furnace atmosphere oxidized the heavy metal; samples with open pores were also contaminated in the interior, which rendered the pre-reduction treatment ineffective. Samples with closed pores were re-oxidized on the surface but remained intact in the interior. Therefore, the possibility of re-oxidation after the reduction must also be carefully excluded, otherwise embrittlement will be encountered even after thorough reduction.

<u>Pre-oxidized samples</u>

To test the effectiveness of the pre-reduction treatment as shown in Fig.21, even in the case of heavily oxidized samples, several standard green samples were oxidized intentionally by heating them in air for 15 min at 420°C until they showed yellow brown and blue colors on the surface. Afterwards some samples were put into the furnace and slowly heated from 500 to 1400°C, the treatment lasting for 6 hrs. Other samples were pushed immediately into the heating zone and cooling were carried out as usual (Tab.5).

<u>Table 5:</u> Properties of sintered samples heated up to sintering temperatures at different rates (green compacts preoxidized) Average values from 4 samples. (W 503/79 , 1480°C, t_s 30 min, slowly cooled)

	Density (g/cm^3)	Hardness Hv 62,5	σ_B (MPa)	Elongation (%)
rapid heating within 30 min	16,871±0,12	286±7	784±17	3,6±0,3
slow heating within 6 hrs	17,080±0,01	299±3	998±9	22,4±1,3

All samples sintered without pre-reduction exhibited large swellings, high porosities and extreme brittleness. As the pressing lubricant had been removed by the oxidizing treatment, the swelling and pore formation must have been caused by evaporation of volatile compounds in the heavy metals, probably tungstic oxides.

The extremely low tensile strengths and elongations of those samples are caused by the poor interphase strength between W-grains and binder. SEM investigations showed clearly the intergranular fracture; the surface of the grains is covered with dark blotches which are most probably oxidic contaminations inhibiting the wetting between binder phase and W grains (Fig.22). Similar phenomena were also observed in earlier investigations (First Annual Report) but always on samples with poor elongations.

On the other hand, the properties of the oxidized and pre-reduced samples were quite similar to those of samples not subjected to oxidizing treatments. The samples were fully dense and tensile strength and elongation reached a very satisfactory level. Investigations of the fracture surface revealed the characteristics of highly ductile samples: transgranular fracture, excellent interphase strength and severe deformation of the binder (Fig.23). It can be concluded, therefore, that thorough pre-reduction treatments also give excellent results in the case of heavily contaminated heavy metals; even heavily oxidized powders may be used for production of these alloys, if a proper pre-reduction treatment is carried out.

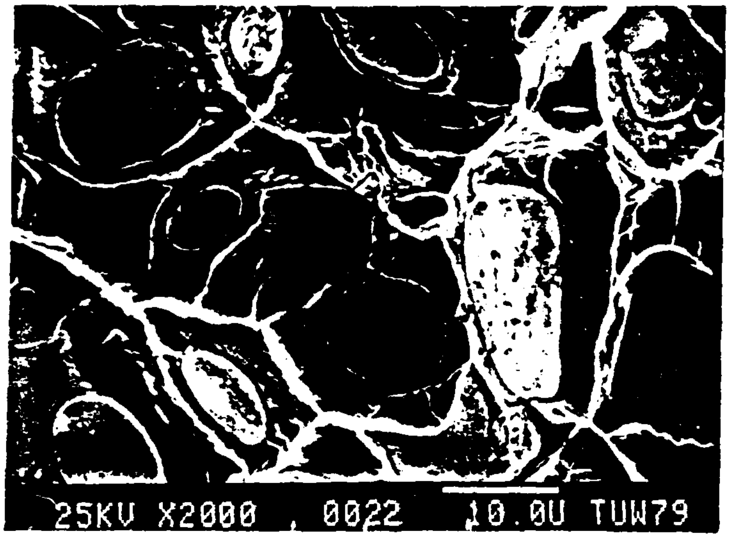


Fig.22: No pre-reduction before sintering

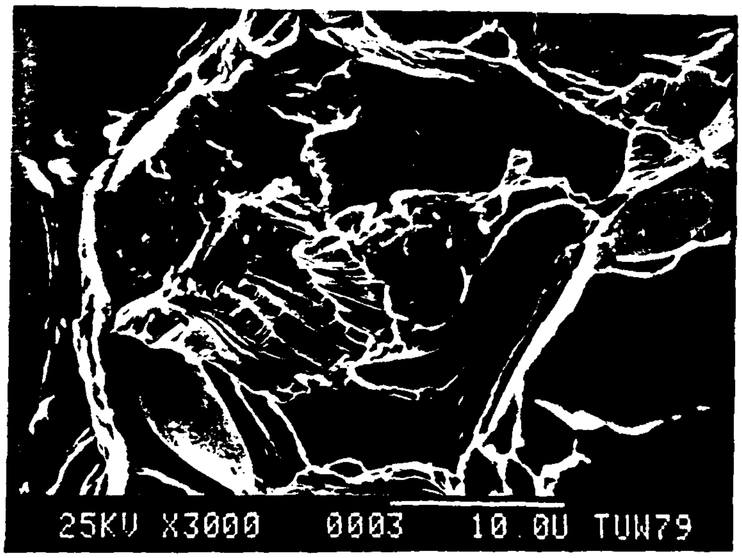


Fig.23: Pre-reduction as shown in Fig.21

Fracture surfaces of W heavy metals intentionally oxidized and then sintered for 30 min at 1470°C

3.4 Influence of the dew point

Regarding the detrimental effect of low O-contents in W heavy metals, the investigation of the influence of oxygen in the H_2-atmosphere, expressed as dew point, was an interesting problem. For the tests, a Casella dewpoint-meter was available.
The gas leaving the furnace had a dew point of 5-15°C. It was suspected that either a leak in the furnace or impure H_2 was responsible for this high H_2O-content. Careful examinations revealed, however, that this high dew point was due to a high temperature reaction of H_2 with the ceramic lining of the furnace to form H_2O. This is illustrated by Fig.24, which shows the dew point as a function of the furnace temperature. The regulation of the dew point was possible only by changing the flow of hydrogen through the furnace, which lowered the dew point to ~ 0°C.

A larger series of sintering tests was performed at different dew points, but at the same sintering conditions. Fig.25 shows the more or less statistical relationship between dew point and elongation. Up to a dew point of + 5°C elongations of more than 20% are obtained; at higher dew points, the probability of obtaining lower elongations is markedly increased.

3.5. Cooling after sintering:

Several authors (1,3) mention that the cooling rate influences the mechanical properties of W heavy metals. R.V.Minakova et al (5) cooled heavy metals slowly to certain temperatures and then quenched them; they found that the samples were more ductile, the lower the temperature from which they were quenched . Within this project, earlier investigations showed

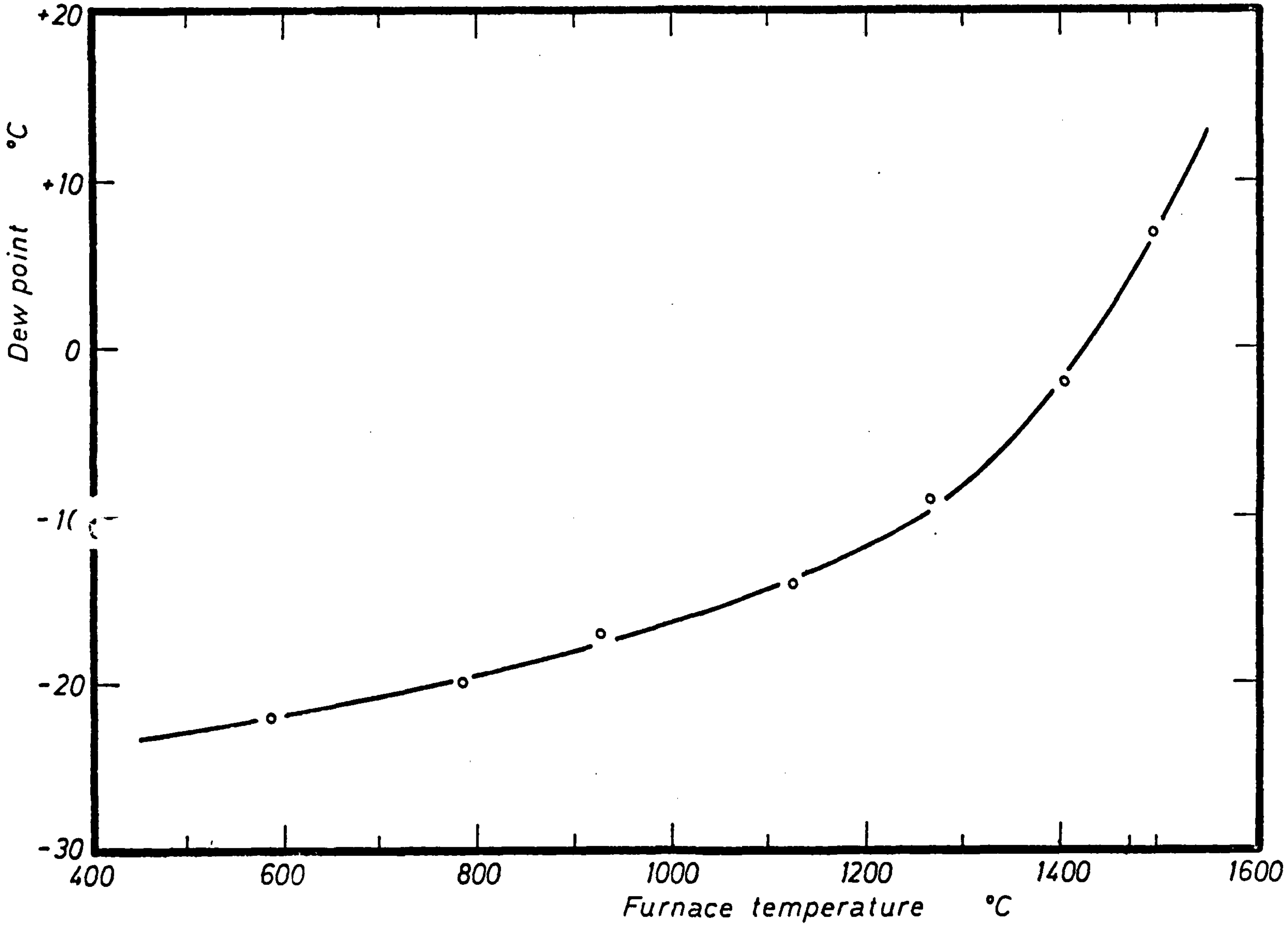


Fig.24: Dew point of the H_2 atmosphere as a function of the furnace temperature

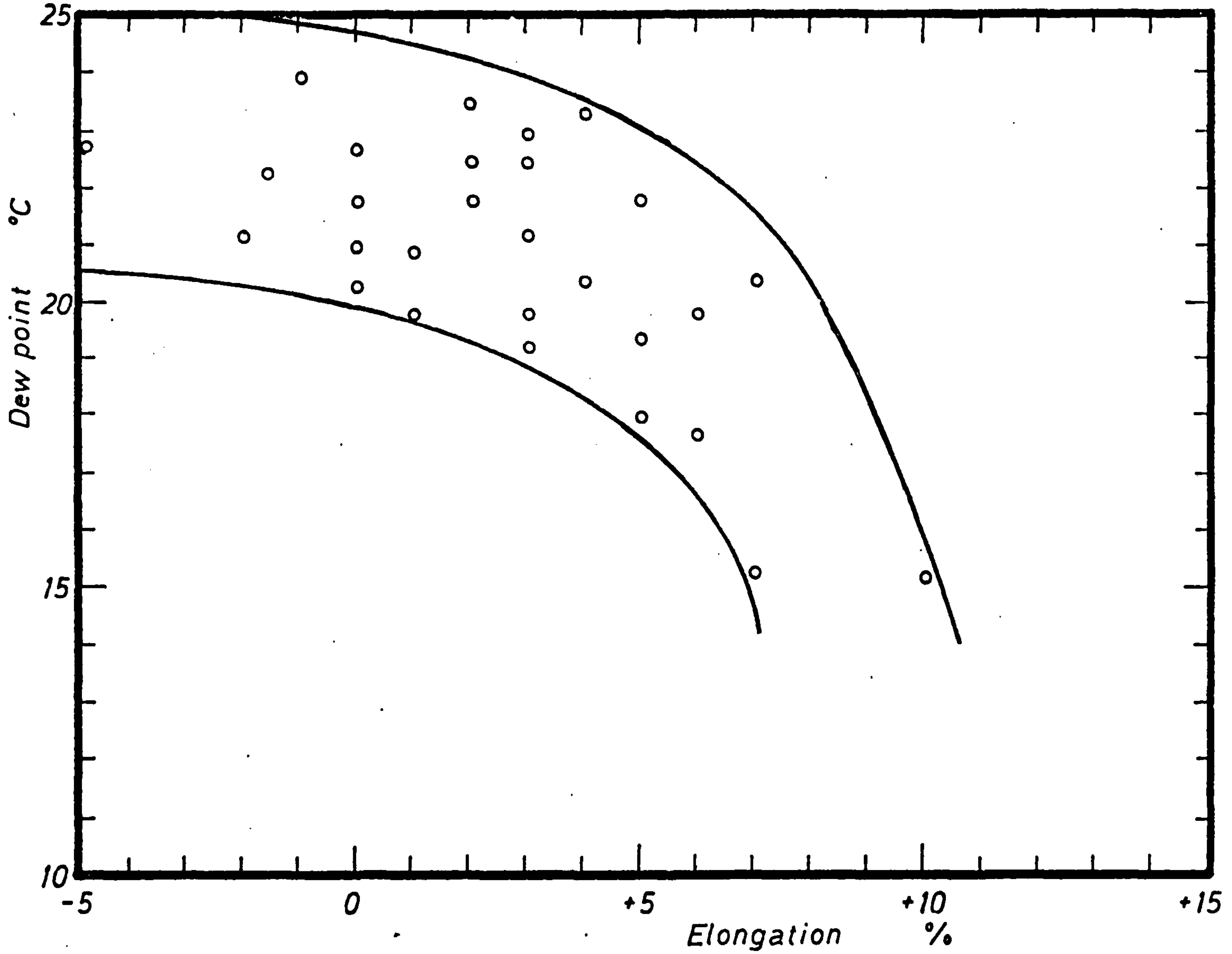


Fig.25: Elongation of sintered samples as a function of the dew point during sintering

that slow cooling in the furnace after sintering doubled the elongation in comparison to rapidly cooled samples. Even in the furnace, however, the samples are cooled rather quickly in the first minutes. It might be of interest to lower the cooling rate during the inital stage of cooling (solidification of the liquid phase). The samples used for these tests were of standard composition and were de-waxed, pre-reduced and sintered as usual (fig.21). Then the furnace was cooled within 30 min from 1475 to 1415°C, afterwards the samples were cooled to room temperature, either in 14 hrs or in 30 min or, by quenching in water, in a few seconds.

Table 6: Properties of sintered samples cooled by different procedures. Pre-reduction as in Fig.21, sintered 30 min at 1475°C.

Cooling	Density g/cm^3	Hardness Hv 62,5	σ_B MPa	Elongation (%)
1475-1415°C in 30 min,	17,115	311	965	22,8
then slow cooling	17,108	308	971	21,3
in the furnace	17,102	314	958	20,9
	17,088	304	981	23,3
1575-1415°C in 30 min,	17,102	299	924	19,6
then quenching in	17,108	303	931	20,2
water	17,112	296	916	18,7
	17,094	298	920	18,8
1475-1415°C in 30 min,	17,094	303	924	18,0
then rapid cooling to	17,092	298	926	19,2
room-temperature in	17,101	306	911	19,8
30 min.	17,088	304	930	17,3

These modified cooling treatments did not result in superior mechanical properties. When cooled in the furnace within 14 hrs, the samples were roughly comparable to those sintered in the usual way (Fig.21), otherwise a certain decrease in tensile strength and elongation was observed. It is evident, however, that samples cooled within 30 min from 1415°C are much more ductile than those cooled in the same manner from sintering temperature; the elongation increased from 12% to 18%. To further investigate this phenomenon, a series of heat treatment tests was carried out.

3.6 Heat treatments:

In the literature, heat treatments are proposed to remedy embrittlements in W heavy metals encountered after sintering, either to remove embrittling phases (1) or to suppress the embrittling influence of hydrogen (2,3). Within this program, the goal was the further improvement of samples with already satisfactory ductility i.e. 24% elongation for 90% W . Standard samples 90% W (503/79), 6,7 Ni, 3,3 Fe were subjected to the usual sintering treatment (fig.21) and then heat treated at different temperatures in H_2 or N_2. Afterwards they were either cooled down in the furnace or quenched in water. Tab.7 shows the results. For comparison purposes the properties of samples sintered in the same batch but not subjected to heat treatment are shown in each group; again the excellent reproducibility of the properties is evident.

Table 7: Properties of samples sintered as in fig.21 and then heat treated. Sintered at 1470°C for 30 min; heat treated for 30 min (Average values from 4 samples)

Temp.of heat treatment °C	Cooling	Density g/cm³	Hardness Hv 62,5	σ_B MPa	Elongation (%)
Treatment in H_2					
800	rapid	17,089	302	941±10	19,2±2,1
	slow	17,091	305	966±12	21,7±0,4
	no treatment	17,088	299	956±5	22,3±1,2
1000	rapid	17,075	306	936±13	14,4±2,2
	slow	17,083	300	955±10	20,4±1,2
	no treatment	17,089	308	953±4	21.0±1,6
1200	rapid	17,067	298	874±38	7,8±1,7
	slow	17,085	305	949±18	21,4±1,3
	no treatment	17,081	303	962±12	21,0±0,8
Treatment in N_2					
800	rapid	17,085	295	947±13	19,6±2,2
	slow	17,084	298	948±18	20,8±1,7
	no treatment	17,093	300	963±10	22.2±0,8
1000	rapid	17,076	310	972±7	19,2±1,8
	slow	17,087	307	970±7	20,8±1,8
	no treatment	17,089	303	967±11	22,8±1,4
1200	rapid	17,079	308	980±8	19,7±2,9
	slow	17,089	304	966±18	22,7±1,7
	no treatment	17,091	309	967±14	22,4±2,2

As shown in the table, in the case of H_2 treatment no improvements over the as-sintered samples were achieved. By cooling in the furnace, roughly the same properties were obtained. Rapid cooling worsened the properties more, the higher the temperature of the heat treatment was; this effect agrees well with the observation of Minakova et al.

The heat treatment in N_2 did not improve the properties, either. There was a marked difference, however, as compared withthe treatment in H_2: after heat treatment in N_2 the cooling rate had hardly any effect to the mechanical properties of the samples. This observation confirms the theory that H_2 can indeed embrittle W heavy metals, but only if the samples are cooled too rapidly to enable the H_2 dissolved in the alloy to escape. At slow cooling rates, the concentration of hydrogen in the heavy metals falls off according to the equilibrium and below 800°C it reaches harmless values.

If this theory is correct, vacuum treatments should not improve the properties of heavy metals cooled slowly after sintering and, as observed with N_2 treatments, the cooling rate would not have any effect either.

To check this, standard samples were sintered as shown in fig.21, then they were heat treated at various temperatures in an induction furnace at 10^{-4} mmHg for 30 min. Together with the properties of the heat treated samples, those of as-sintered samples from the same batch are shown.

As expected, no effect of the vacuum heat treatment could be observed; the values of heat treated and as-sintered samples were almost identical. Even the elongation, which is very sensitive to all changes in the production cycle, was not influenced. This would indicate that vacuum treatments are not necessary to obtain good elongations if the cooling after sintering has been slow enough to permit removal all excess hydrogen from the heavy metals.

Table 8: Properties of samples sintered in Fig.21 and then vacuum treated as compared to untreated samples. Sintered 30 min at 1470°C, heat treated for 30 min. (Average values from 4 samples)

Temp.of heat treatment °C	Cooling	Density g/cm^3	Hardness Hv 62,5	MPa	Elongation (%)
1000	rapid	17,091	308	952±6	22,7±1,2
	slow	17,083	309	945±2	21,5±1,5
	no treatment	17,081	307	952±11	22,2±1,6
1200	rapid	17,089	308	976±10	23,4±0,8
	slow	17,096	306	998±3	24,0±1,0
	no treatment	17,094	311	981±8	25,0±0,7

4. Influence of impurities on the mechanical properties

4.1 Metal additives to the binder

As mentioned in the introduction, numerous experiments have been described in the literature for improving the properties of heavy metals by adding other metals to the binder - first with W-Ni-Cu heavy metals (6), then, after the replacement of Cu by Fe (7), also in the then new W-Ni-Fe-metals (8). Addition of 30% Co to the binder has been found advantageous (9), Cr increases the hardness, but lowers the ductility considerably (10). Since most of these additives were in the range of several wt%, it was hoped that a marked decrease in the amount of additives would either given positive effects on some properties but suppress negative effects on others, or would largely retain the positive effect and simply make it possible to save rare and expensive metals. To that end, 0,5 and 0,05 wt% of six metals were added to the W-Ni-Fe mixture: Cr, Mo, Co, V and Cu, which had been used already in earlier experiments (see First Annual Rep.) and Mn. Cr was added as ferro chromium (12,5 wt% Cr), all other metals as pure powders. All were sieved to remove grains >50 um. The preparation of the samples was carried out in the usual manner; the powders were mixed in Cyclohexane with 1% Camphor for 3 hrs, granulated and then pressed with 5,15 ton/cm^2. The green samples were sintered at 1470°C for different lengths of time to reveal any accelerating effects of the additives or the sintering process.

To ensure reliability and reproducibility of the experiments, in every sintering boat 6 samples with additives, 2 of each powder charge and 2 standard composition samples were sintered, arranged as in Fig.26. As our tests had shown, 4 parallel samples are sufficient to give reliable mean values.

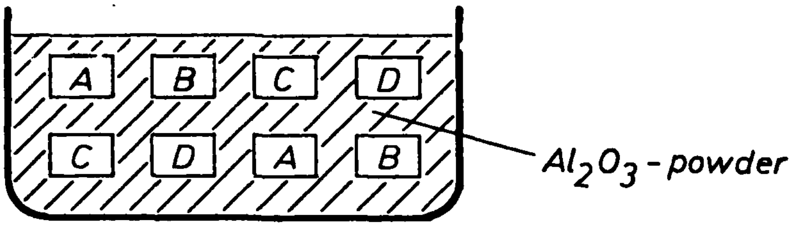


Fig.26: Arrangement of the bars in the sintering boat

Table 9: Mechanical properties of heavy metals with metal additives to the binder. 90% W, Ni:Fe=2:1; sintered as in Fig.21 at 1470°C (Average values from 4 samples).

Additive	Sintering time (min)	Density g/cm³	Hardness Hv 62,5	σ_B MPa	Elongation (%)
0,5% Cr	15	17,050	312	977±15	18,1±2,1
	30	17,108	308	921±9	13,9±2,9
	60	17,117	303	853±13	9,9±1,8
0,5% Mo	15	17,123	311	966±16	18,7±0,6
	30	17,128	310	950±23	23,3±1,7
	60	17,113	304	921±11	20,5±1,8
0,5% Co	15	17,117	305	938±8	24,1±0.6
	30	17,115	300	958±6	24,2±0,9
	60	17,117	298	922±14	24,2±1,2
0,5% Cu	15	17,107	298	947±4	14,8±1,0
	30	17,113	292	902±12	12,3±1,7
	60	17,103	296	895±17	11,3±2,3
0,5% V	15	14,341	297	708±24	1,9±0,4
	30	14,714	306	735±18	5,7±2,8
	60	15,218	299	774±31	7,0±1,9
0,5% Mn	15	17,075	302	919±10	11,3±0,5
	30	17,081	311	869±5	10,9±1,0
	60	17,088	308	849±9	11,3±0,8

Table 9: (continued)

Additive	Sintering time(min)	Density g/cm^3	Hardness Hv 62,5	σ_B MPa	Elongation (%)
0,05% Cr	15	17,103	308	991±5	22,3±2,1
	30	17,099	313	922±11	20,9±0,7
	60	17,081	311	937±7	14,2±0,5
0,05% Mo	15	17,114	311	983±8	22,0±2,0
	30	17,098	314	953±17	23,6±1,5
	60	17,099	308	918±13	20,5±1,8
0,05% Co	15	17,091	307	974±8	21,2±0,8
	30	17,084	311	921±7	20,3±1,7
	60	17,089	311	938±17	11,3±1,6
0,05% Cu	15	17,084	308	956±5	22,2±1,9
	30	17,097	314	949±16	19,3±1,7
	60	17,082	310	922±16	10,6±1,1
0,05% V	15	16,143	297	742±32	2,1±1,1
	30	16,110	292	738±24	5,9±1,8
	60	16,471	301	913±19	8,0±2,7
0,05% Mn	15	17,084	305	976±4	23,6±1,6
	30	17,097	310	956±9	17,3±1,1
	60	17,103	314	958±8	16,4±1,9

The samples containing V showed large swellings both with 0,5 and 0,05% V; pore channels seemed to run through all the test bars. Apparently a chemical compound forms which begins to evaporate at sintering temperature; because of the liquid phase the vapor can not escape from the bar but forms pores inside the samples. Understandably the mechanical properties of these samples were very poor and the tensile strength values were very widely scattered as compared to the other series.

Addition of 0,5% of other metals did not improve the properties of the heavy metals as compared to the standard W-Ni-Fe alloys. Only Co improved the ductility somewhat an effect observed earlier with higher Co contents (9).

The lower percentage of additives, 0,05% resulted in the same values as achieved with standard composition, but only at the rather short sintering time of 15 min. At longer sintering times the elongation was reduced by Cu and surprisingly by Co by more than 50%. The embrittlement caused by 0,5% Cr and Mn was considerably reduced here; at 15 min. sintering time properties equal to the standard were measured. In no case could any improvement be realized.

Except for the samples containing V, the reproducibility was hardly affected by the metal additives and was quite comparable to that of heavy metals with Ni-Fe binder.

Metallographic investigations:

From metallographic samples etched with $CuSo_4/NH_3$ solution, average grain sizes were determined by counting the grains on 0,6 mm long strips and calculating the grain size after taking into account the area due to binder. From each sample 9 strips were measured. With this test length, a surprisingly good rate of reproducibility was achieved. Tab.10 shows the average grain sizes thus obtained.

Tab.10: Average grain sizes of heavy metals with metal additives to the binder at different sintering times (in um)

0,5% additive	15 min	30 min	60 min
Cr	16,1	18,0	22,0
Mo	16,7	19,5	22,3
Co	19,4	20,3	23,6
Cu	18,5	21,4	24,2
V	19,8	21,5	23,6
Mn	18,2	21,5	22,5
(Standard)	18,7	20,7	23,1
0,05% additive			
Cr	18,3	20,2	22,6
Mo	18,9	21,2	23,7
Co	19,4	21,4	24,2
Cu	19,7	20,9	23,8
V	20,0	22,1	24,4
Mn	18,1	20,5	23,7
(Standard)	19,2	21,3	24,0

It seems that Cr and Mo inhibit grain growth, while V and to a lesser extent, Co, promote it . A definite connection between grain size and mechanical properties could not be derived; only the decline of ductility with grain coarsening was confirmed.

Summarizing, it can be stated that within the elements and concentration range examined small amounts of the investigated metals do not result in significant improvements in W heavy metal properties. In most cases deterioration of the mechanical properties was observed. Such positive effects as that of e.g. Cr on the ductility of heavy metals, as mentioned in the First Annual Report apparently are due only to its deoxidizing ability. Thorough de-oxidation renders it useless and sometimes even harmful.

4.2 Heavy metals sintered from W powers doped with trace impurities

In accordance with our request, 14 special W powders were produced to be compared to the standard powder W503/79. Most of these powders contained small amounts of special impurities which represented those contaminations most likely to be present in commercial W powders. The powder E30W was prepared from impure blue oxide and E33 was not doped at all for an estimation of the differences between various undoped powders.

The production of the green compacts was carried out as described above. The powders were compacted with a pressure of 5,15 ton/cm^2. No difficulties, such as pressing faults, were encountered, except with powder E8W, which at first resulted in horizontal cracks. A second granulation of the green compacts and subsequent pressing resulted in faultless samples. These difficulties probably had been caused by the unsatisfactory flow behavior of the powder; instead of flowing uniformly, the powder mixture formed lumps which caused inhomogeneous filling of the die and in due course tensions in the green compacts which caused them to crack. This tendency to form lumps had been observed earlier and was the source of trouble with fine powders (see First Annual Report).

For the sintering of the samples, the sintering cycle found to be optimal in earlier investigations was selected (First Annual Report, Sintering Cycle Fig.2). The temperature-time diagram is shown in Fig.21. After a 60 min de-waxing treatment at 500°C, thorough pre-reduction ensured complete removal of oxygen. For that purpose the furnace was heated in 6 hrs from 500 to 1400°C. At that temperature, the Mo boats containing the samples was pulled into a somewhat cooler section of the furnace and was then pushed back into the heating zone when the furnace had reached sintering temperature. The sintering time could thus be determined very exactly. After sintering, the furnace was simply switched off. It cooled down to 500°C in 14 hrs at which temperature the boat was pulled stepwise out of the furnace.

To enable a meaningful comparison between the samples prepared from doped W powders and those prepared from standard W503/79, 4 doped samples and 4 standard bars, arranged in a checker board pattern to compensate for all possible differences in temperature distribution during the sintering process, were sintered in every batch (Fig.27). To give reliable average results, at least 10 samples were prepared and tested from each powder. This was necessary because the difference, especially for the elongations, between standard and doped samples was sometimes hardly detectable.

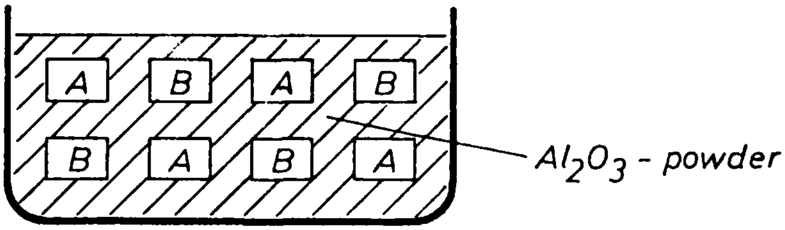


Fig.27: Arrangement of the bars in the sintering boat

To further illustrate the scatter in the values for tensile strength and elongation, the results were evaluated using Weibull-statistics (11). From a certain number of values, the probability of fracture at a given stress can be derived. On the other hand, it is possible to determine the stress which would cause 50% of the samples to break.

The probability of fracture (P) is influenced by the sample volume (V) , tensile strength (σ) and a parameter indicating the homogeneity of the material (m), following the equation

$$P = 1 - 1/\exp. \frac{V}{V_o} \cdot \left(\frac{\sigma}{\sigma_0}\right)^m$$ (V_o, σ_o refer to standard sample)

The equation is then transformed and σ_{50} inserted

$$\lg\lg \frac{1}{1-P} - \lg\lg 2 = m \; . \; (\lg\sigma - \lg \sigma_{50})$$

For a given amount N of samples, the P values depend only on the sample number n (from 1 to N). The graphic evaluation is carried out by taking the left side of the equation for the x-values and the right for y-values.

$$x = \lg\lg \frac{1}{1-P} \quad \text{and with } P_n = \frac{n}{N+1}$$

$$x = \lg\lg \frac{N+1}{N+1-n}$$

$$y = \lg\sigma$$
$$s_w = 1/m$$

This is the equation of a straight line

$$y - y_{50} = s_w \cdot (x - x_{50})$$

The slope of the Weibull straight line indicates the scatter of the individual values; the broader the scatter, the more pronounced the slope and the greater the probability of fractures occurring below the average tensile strength.These statistics take into account the imperfections in the individual samples which are the main initiators of fracture. The probability of fracture at a given stress is determined by number, distribution and kind of imperfections. The Weibull statistics have been used successfully in many cases and for a given purpose are usually more reliable than the usual Gaussian distribution. In the following tables the arithmetic means and standard deviations for all properties are shown after the individual values. For each charge with values from doped and standard samples the Weibull-diagrams for tensile strength and elongation are also given.

Powder E2 (250 ppm Na)

Table 11: Mechanical properties of the samples prepared from E2 and of the comparison samples from 5O3

	E 2				5o3			
ST TP °C °C	ρ g/cm³	σ_B MPa	δ %	H_V	ρ g/cm³	σ_B MPa	δ %	H_V
147o + 2	17,1o63	962	24,o	3o7	17,o931	943	21,4	292
	17,o971	955	22,6	299	17,1o6o	955	22,o	292
	17,1o84	964	23,o	3o5	17,o887	948	2o,o	294
	17,o962	946	2o,4	291	17,o899	943	18,8	298
1475 + 3	17,1o44	943	23,6	3o3	17,o941	936	2o,2	299
	17,o826	944	21,6	3o4	17,o988	962	23,6	296
	17,o751	95o	25,2	293	17,o866	962	26,2	293
	17,o9o5	948	21,6	3o4	17,o815	964	19,2	298
1475 + 3	17,o759	945	22,6	3o1	17,o8o3	96o	22,8	296
	17,o936	973	21,4	3o6	17,o854	948	2o,6	296

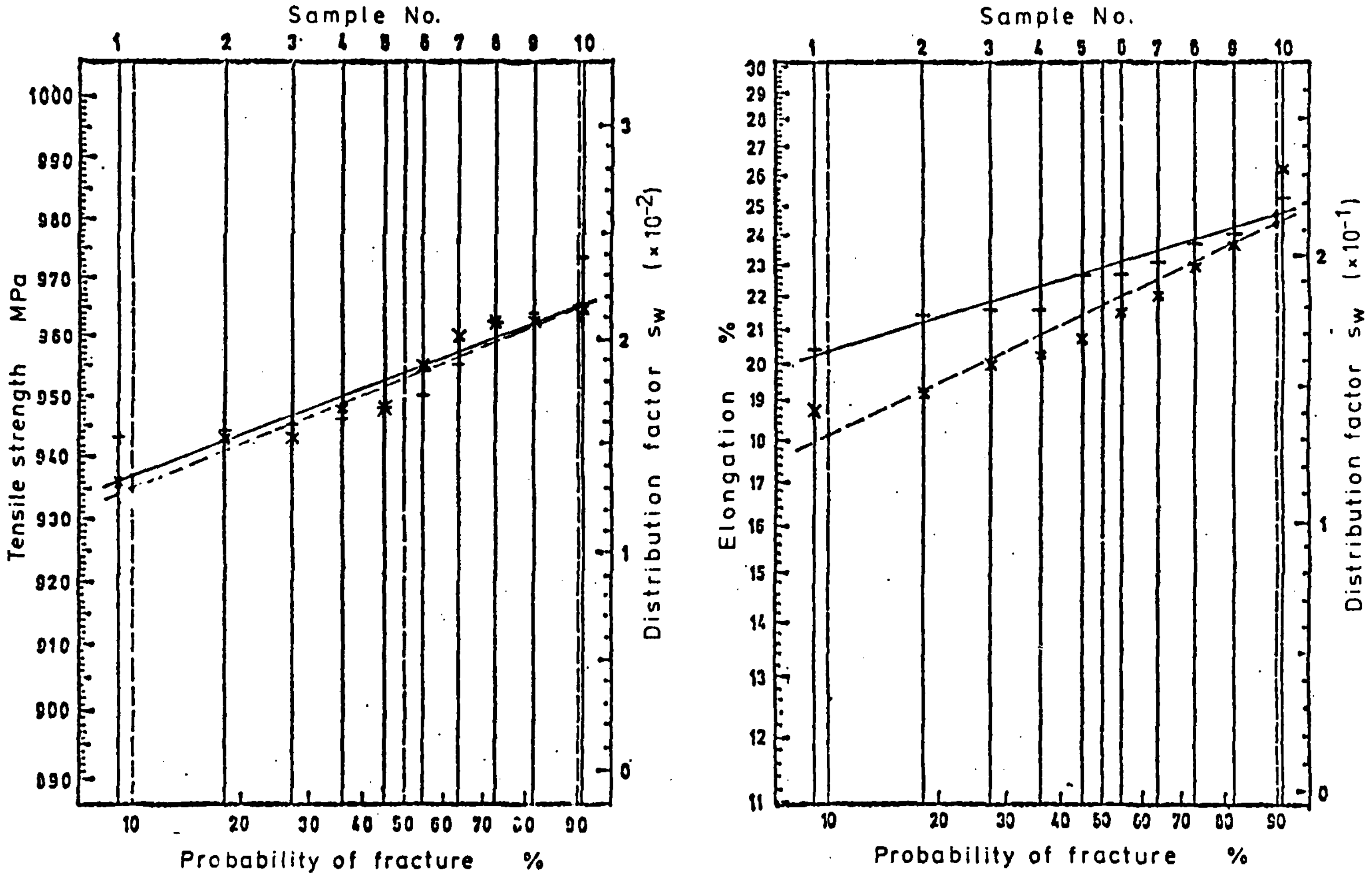
Mean values ± standard deviations

	ρ_{Gr} g/cm³	ρ g/cm³	SS %	H_V	σ_{5o} MPa	s_σ $.1o^{-2}$	δ_{5o} %	s_δ $.1o^{-2}$
E 2	12,o2 ± o,o1	17,o9 ± o,o1	29,7	3o2 ± 5	954	o,947	22,7	6,o57
5o3	11,7o ± o,o2	17,o9 ± o,o1	31,5	295 ± 3	953	1,oo2	21,6	9,56o

ST .. Sintering temperature
TP .. Dew point
ρ_{Gr} .. density of green sample
ρ .. density of sintered sample

SS .. Shrinkage during sintering
s_σ, s_δ .. slope values of the Weibull straight lines

Fig.28: Weibull-Diagrams for powder E2



solid line and - for powder E2

broken line and x for standard powder W503

Powder E5 (250 ppm Li)

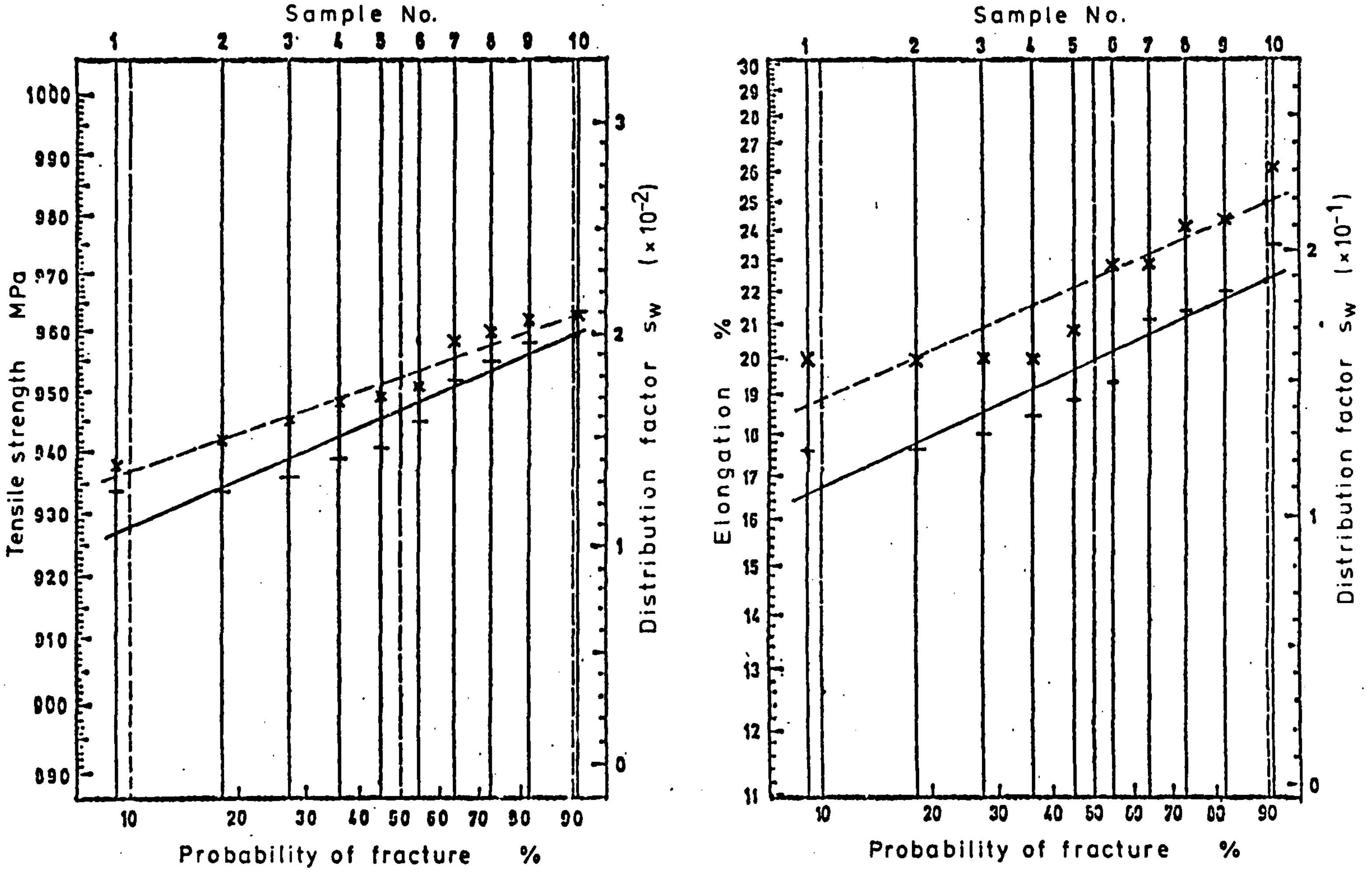
Table 12: Mechanical properties of the samples prepared from E5 and of the comparison samples from 5O3

	E 5				5o3			
ST TP °C °C	ρ g/cm³	σ_B MPa	δ %	H_V	ρ g/cm³	σ_B MPa	δ %	H_V
147o + 5	17,o914	934	18,o	29o	17,o837	948	22,8	296
	17,o938	939	18,4	292	17,o736	945	2o,o	3o2
	17,1o23	945	21,4	297	17,1o34	958	2o,o	299
	17,1o68	958	19,4	292	17,o844	951	2o,o	298
148o + 4	17,1o42	934	17,6	297	17,o899	942	2o,8	295
	17,1o68	941	18,8	297	17,o958	938	2o,o	293
	17,1o58	955	22,o	3o1	17,o957	949	24,o	3o1
	17,o94o	964	23,4	3o2	17,o935	962	24,4	298
148o + 5	17,o788	936	17,6	296	17,o866	962	26,2	293
	17,o853	952	21,1	291	17,o8o3	96o	22,8	296

Mean values ± standard deviations

	ρ_{Gr} g/cm³	ρ g/cm³	SS %	H_V	σ_{5o} MPa	s_σ $.1o^{-2}$	δ_{5o} %	s_δ $.1o^{-2}$
E 5	12,31 ± o,o2	17,1o ± o,o1	28,o	295 ± 4	947	1,o63	19,9	9,523
5o3	11,7o ± o,o1	17,o9 ± o,o1	31,5	297 ± 3	953	o,898	22,3	9,oo8

Fig.29: Weibull-Diagrams for powder E5



solid line and - for powder E5

broken line and x for standard powder W503

Powder E8 (188 ppm Ca)

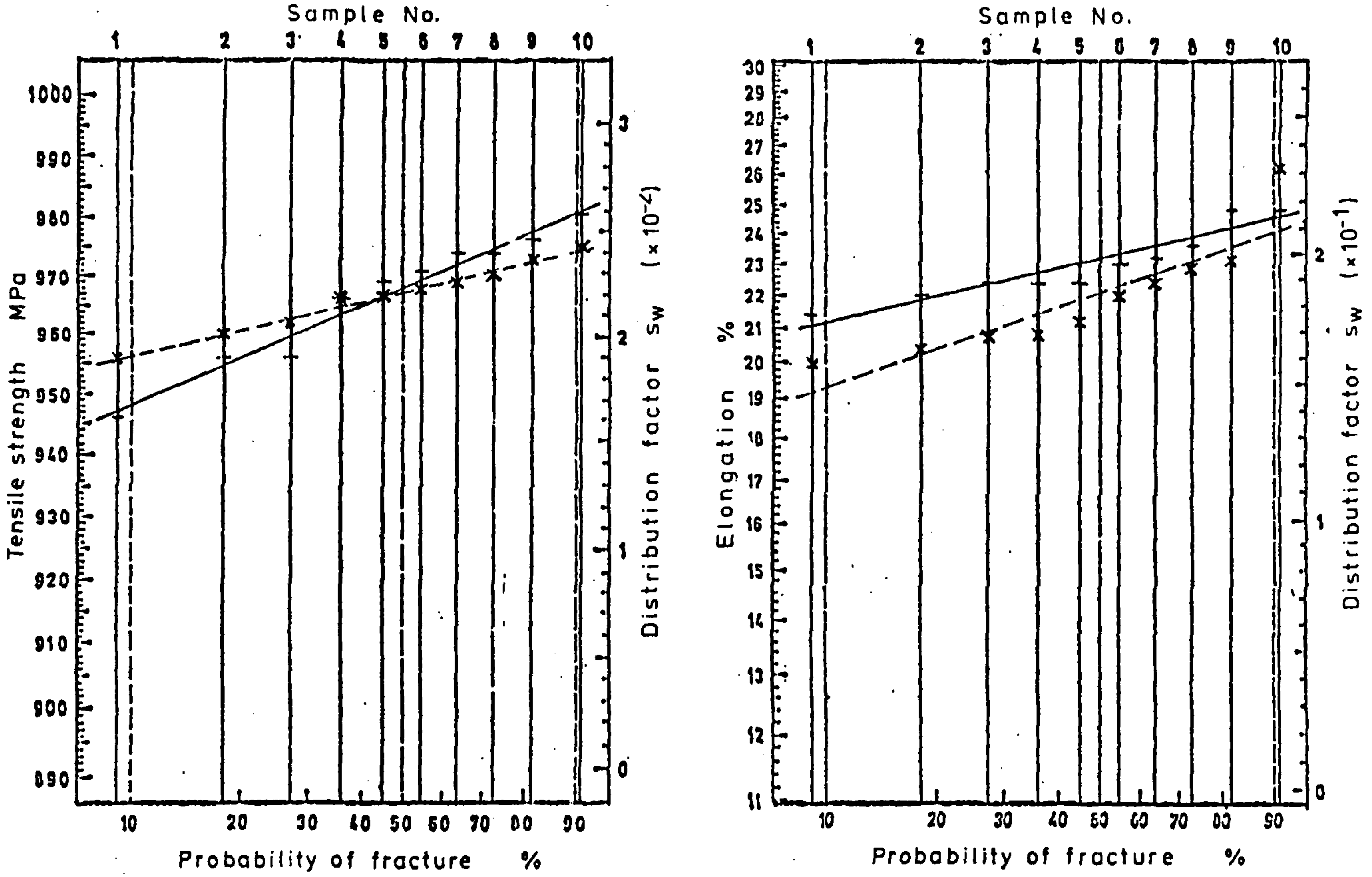
Table 13: Mechanical properties of the samples prepared from E8 and of the comparison samples from 5o3

		E 8				5o3			
ST °C	TP °C	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
147o	+ 3	17,o556	981	22,4	294	17,o855	968	2o,8	298
		17,o657	946	22,4	292	17,o75o	955	2o,o	295
		17,o627	974	22,o	294	17,o923	966	23,o	297
		17,o722	976	23,2	299	17,o955	969	21,2	294
1475	+ 3	17,o34o	956	21,2	299	17,o762	966	2o,8	297
		17,o523	966	23,o	294	17,o611	973	22,o	299
		17,o614	956	22,4	3o2	17,o454	975	22,4	292
		17,o437	974	24,8	299	17,o681	97o	2o,4	292
148o	+ 5	17,o251	971	24,8	3oo	17,o866	962	26,2	296
		17,o311	969	23,6	297	17,o8o3	96o	22,8	293

Mean values ± standard deviations

	ρ_{Gr} g/cm^3	ρ g/cm^3	SS %	H_V	σ_{5o} MPa	s_σ $.1o^{-2}$	δ_{5o} %	s_δ $.1o^{-2}$
E 8	11,73 ± o,o2	17,o5 ± o,o2	31,2	297 ± 3	968	1,115	23,1	4,773
5o3	11,7o ± o,o2	17,o8 ± o,o1	31,5	295 ± 2	967	o,6o2	22,1	7,o45

Fig.30: Weibull-Diagrams for powder E8



solid line and - for powder E8
broken line and x for standard powder W503

Powder E11 (250 ppm B)

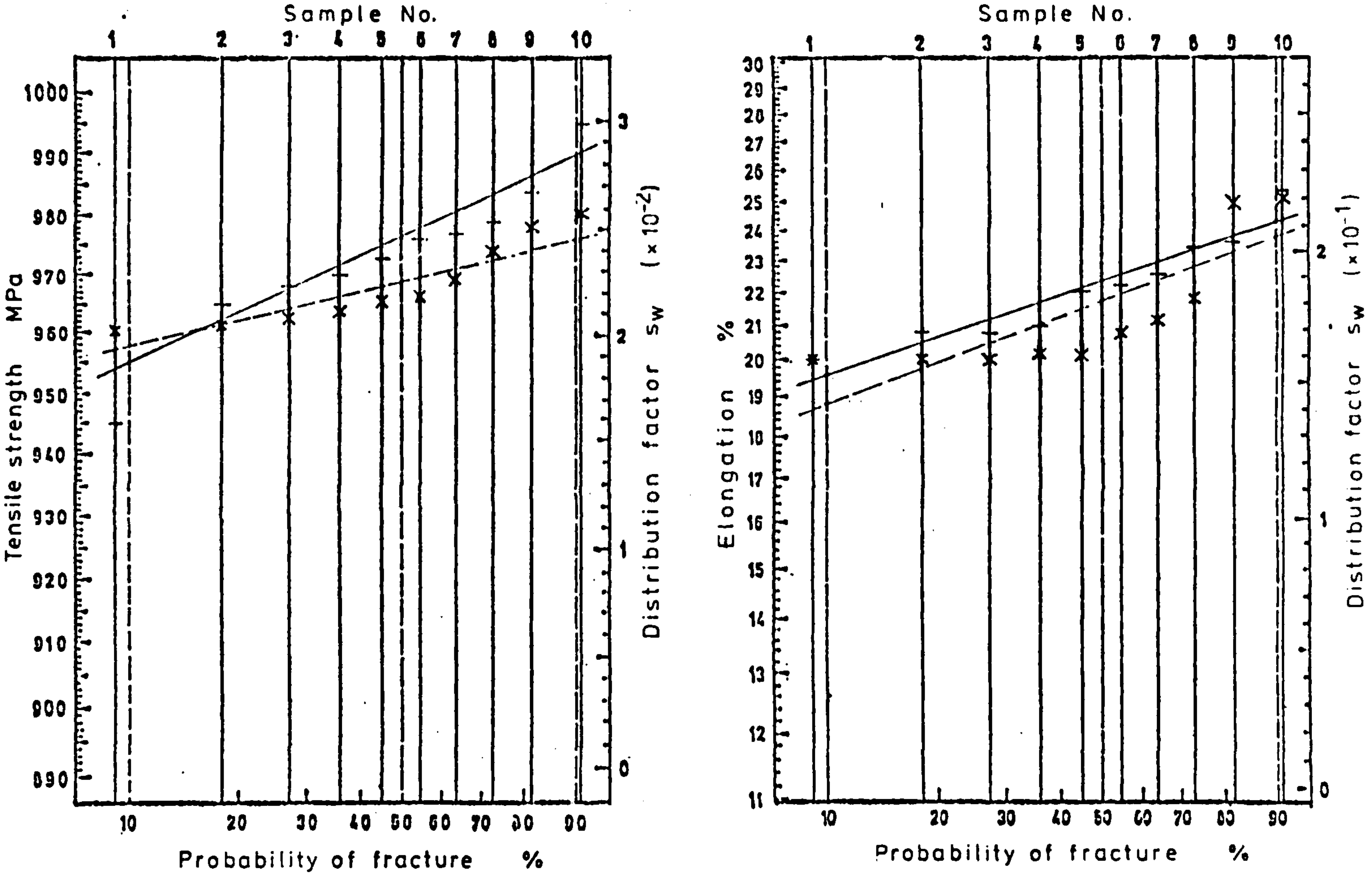
Table 14: Mechanical properties of the samples prepared from E11 and of the comparison samples from 503

	E 11				503			
ST TP °C °C	ρ g/cm³	σ_B MPa	δ %	H_V	ρ g/cm³	σ_B MPa	δ %	H_V
1470 + 3	17,0652	995	25,4	291	17,0727	964	20,0	292
	17,0711	977	22,6	289	17,0577	966	20,0	297
	17,0776	979	22,0	289	17,0574	963	20,2	292
	17,0638	970	21,0	290	17,0606	978	20,0	299
1480 + 2	17,0781	984	20,8	291	17,0623	969	21,8	287
	17,0648	973	23,4	290	17,0600	961	21,2	295
	17,0765	968	20,0	291	17,0618	974	25,0	292
	17,0905	976	22,2	900	17,0655	980	20,8	295
1475 + 5	17,0634	945	20,8	302	17,0708	965	25,2	295
	17,0671	965	23,6	298	17,0798	960	20,2	297

Mean values ± standard deviations

	ρ_{Gl} g/cm³	ρ g/cm³	SS %	H_V	σ_{50} MPa	s_σ $.10^{-2}$	δ_{50} %	s_δ $.10^{-2}$
E 11	10,94 ± 0,04	17,07 ± 0,01	35,9	293 ± 5	976	1,168	22,3	6,863
503	11,70 ± 0,01	17,06 ± 0,01	31,4	294 ± 3	957	0,667	21,5	7,185

Fig.31: Weibull Diagrams for powder E11



solid line and - for powder E11

broken line and x for standard powder W503

Powder E14 (250 ppm Al)

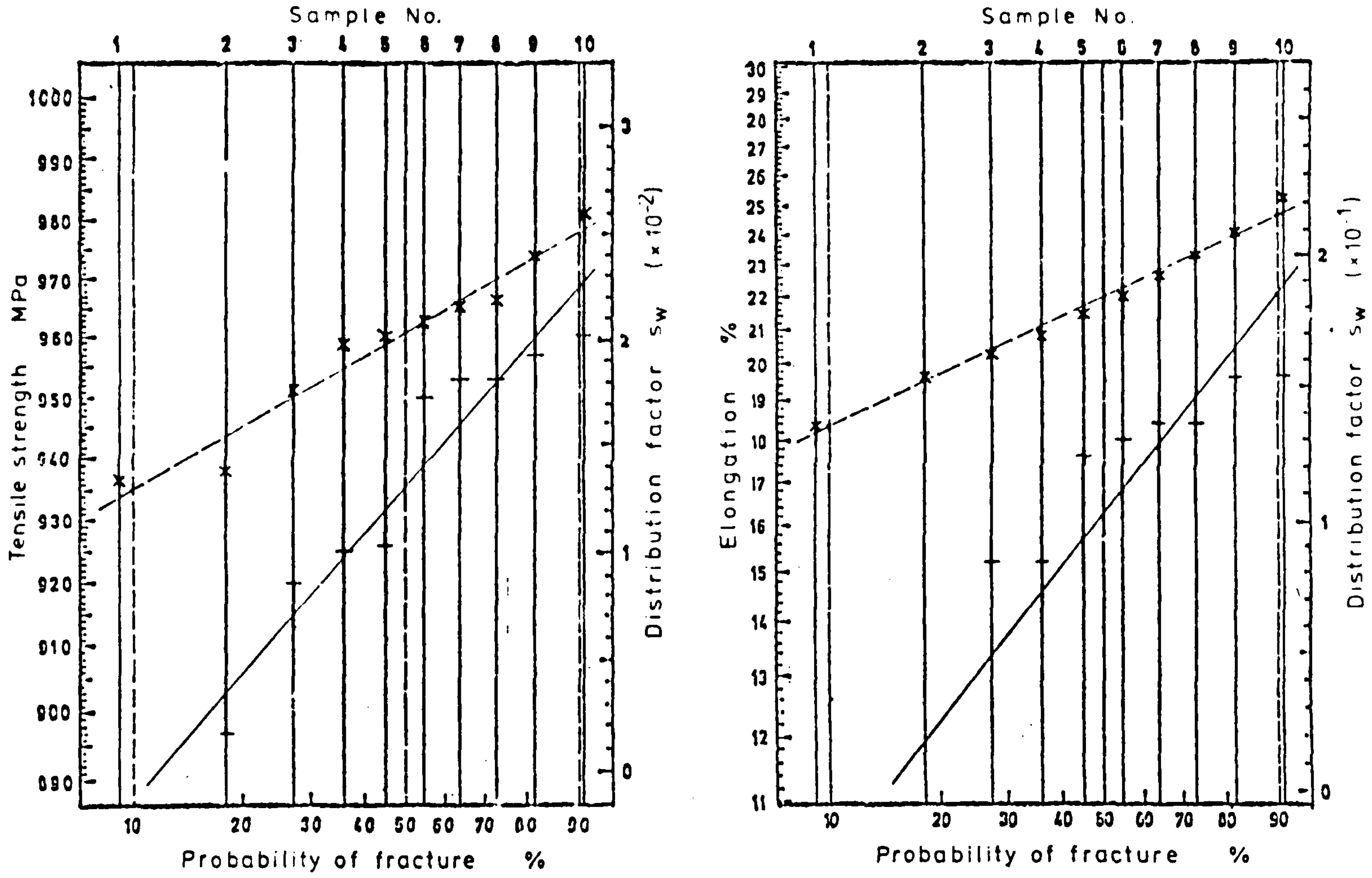
Table 15: Mechanical properties of the samples prepared from E14 and of the comparison samples from 503

	E 14				503			
ST TP °C °C	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
1475 + 2	17,0333	953	15,2	292	17,0708	974	22,6	297
	17,0402	960	18,4	295	17,0736	963	18,4	299
	17,0359	957	18,0	297	17,0862	981	23,2	293
	17,0494	953	19,6	295	17,0802	966	24,0	295
1475 +3	17,0387	897	10,8	292	17,0708	965	25,2	295
	17,0312	950	17,6	300	17,0798	960	20,2	297
	17,0396	881	8,8	290	17,0650	937	19,6	296
	17,0299	925	15,2	290	17,0433	959	20,8	293
1475 + 2	17,0478	920	19,6	293	17,0941	951	22,0	297
	17,0491	926	18,4	297	17,0883	938	21,4	296

Mean values ± standard deviations

	ρ_{Gr} g/cm^3	ρ g/cm^3	SS %	H_V	σ_{50} MPa	s_σ $.10^{-2}$	δ_{50} %	s_δ $.10^{-2}$
E 14	11,56 ± 0,01	17,04 ± 0,01	32,2	294 ± 3	935	2,866	16,2	25,368
503	11,70 ± 0,01	17,07 ± 0,01	31,5	296 ± 2	959	1,440	21,7	9.554

Fig.32: Weibull Diagrams for powder E14



solid line and - for powder E14
broken line and x for standard powder W503

Powder E17 (100 ppm Si)

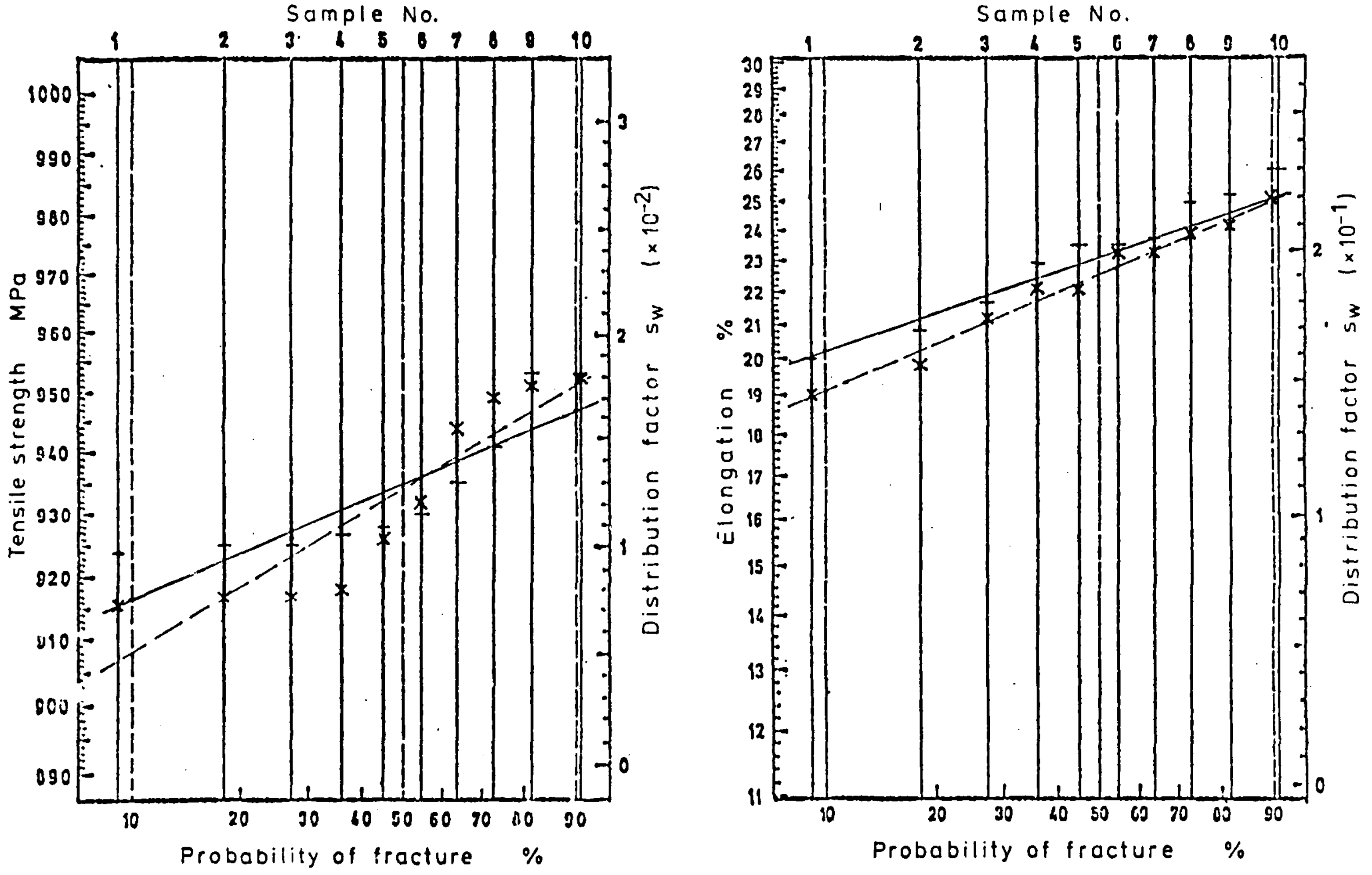
Table 16: Mechanical properties of the samples prepared from E17 and of the comparison samples from 503

		E 17				503			
ST °C	TP °C	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
1485	+ 7	17,0321	924	21,6	297	17,0468	926	24,0	296
		17,0117	928	20,0	302	17,0538	932	23,2	292
		17,0230	925	24,8	291	17,0514	918	19,8	298
		17,0392	927	26,0	290	17,0336	917	19,0	293
1490	+ 3	17,0176	924	22,8	302	17,0329	916	21,0	296
		17,0444	930	23,4	291	17,0385	917	25,0	295
1480	+ 3	17,0285	953	23,6	292	17,0659	944	23,2	292
		17,0448	941	25,2	292	17,0676	951	22,0	292
		17,0625	953	23,4	295	17,0609	949	23,8	287
		17,0499	935	20,8	292	17,0502	952	22,0	291

Mean values ± standard deviations

	ρ_{Gr} g/cm^3	ρ g/cm^3	SS %	H_V	σ_{50} MPa	s_σ $.10^{-2}$	δ_{50} %	s_δ $.10^{-2}$
E 17	11,76 ± 0,01	17,04 ± 0,02	31,0	294 ± 5	935	1,041	23,0	6,942
503	11,70 ± 0,01	17,05 ± 0,01	31,4	293 ± 3	934	1,500	22,5	8,694

Fig.33: Weibull Diagrams for powder E17



solid line and - for powder E17

broken line and x for standard powder W503

Powder E21 (140 ppm Na, 100 ppm P)

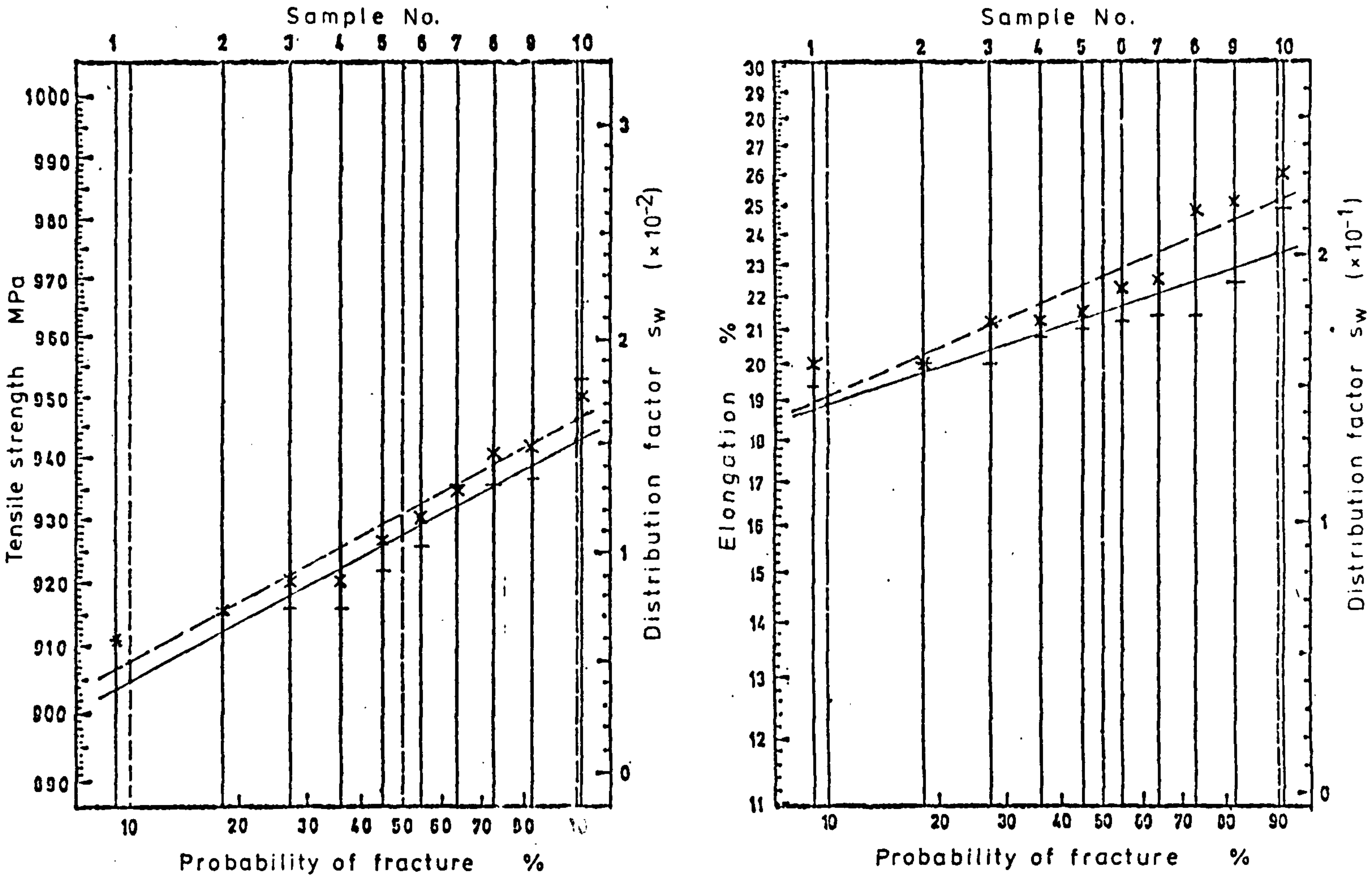
Table 17: Mechanical properties of the samples prepared from E21 and of the comparison samples from 503

		E 21				5o3			
ST °C	TP °C	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
1485	+ 2	17,o95o	911	21,4	297	17,o942	92o	22,2	29o
		17,o79o	936	22,4	3o2	17,o715	911	26,o	291
		17,o81o	916	25,8	289	17,o749	92o	22,4	297
		17,1o14	937	2o,o	292	17,o7o1	942	24,8	289
1485	+ 2	17,o848	953	21,4	289	17,1oo4	935	21,2	294
		17,o752	926	19,4	289	17,o99o	95o	21,4	297
		17,o785	936	2o,8	292	17,o615	941	2o,o	291
		17,1oo8	922	2o,o	292	17,o38o	927	21,2	292
149o	+ 3	17,o555	916	21,6	289	17,o498	93o	2o,o	295
		17,o713	915	21,o	3oo	17,o385	917	25,o	295

Mean values ± standard deviations

	ρ_{Gr} g/cm^3	ρ g/cm^3	SS %	H_V	σ_{5o} MPa	s_σ $.1o^{-2}$	δ_{5o} %	s_δ $.1o^{-2}$
E 21	11,8o ± o,o3	17,o8 ± o,o1	3o,9	292 ± 4	928	1,319	21,5	6,769
5o3	11,7o ± o,o1	17,o7 ± o,o2	31,5	293 ± 3	931	1,31o	22,6	8,655

Fig.34: Weibull Diagrams for powder E21



solid line and - for powder E21

broken line and x for standard powder W503

Powder E24 (je 100 ppm As, Sb, Bi)

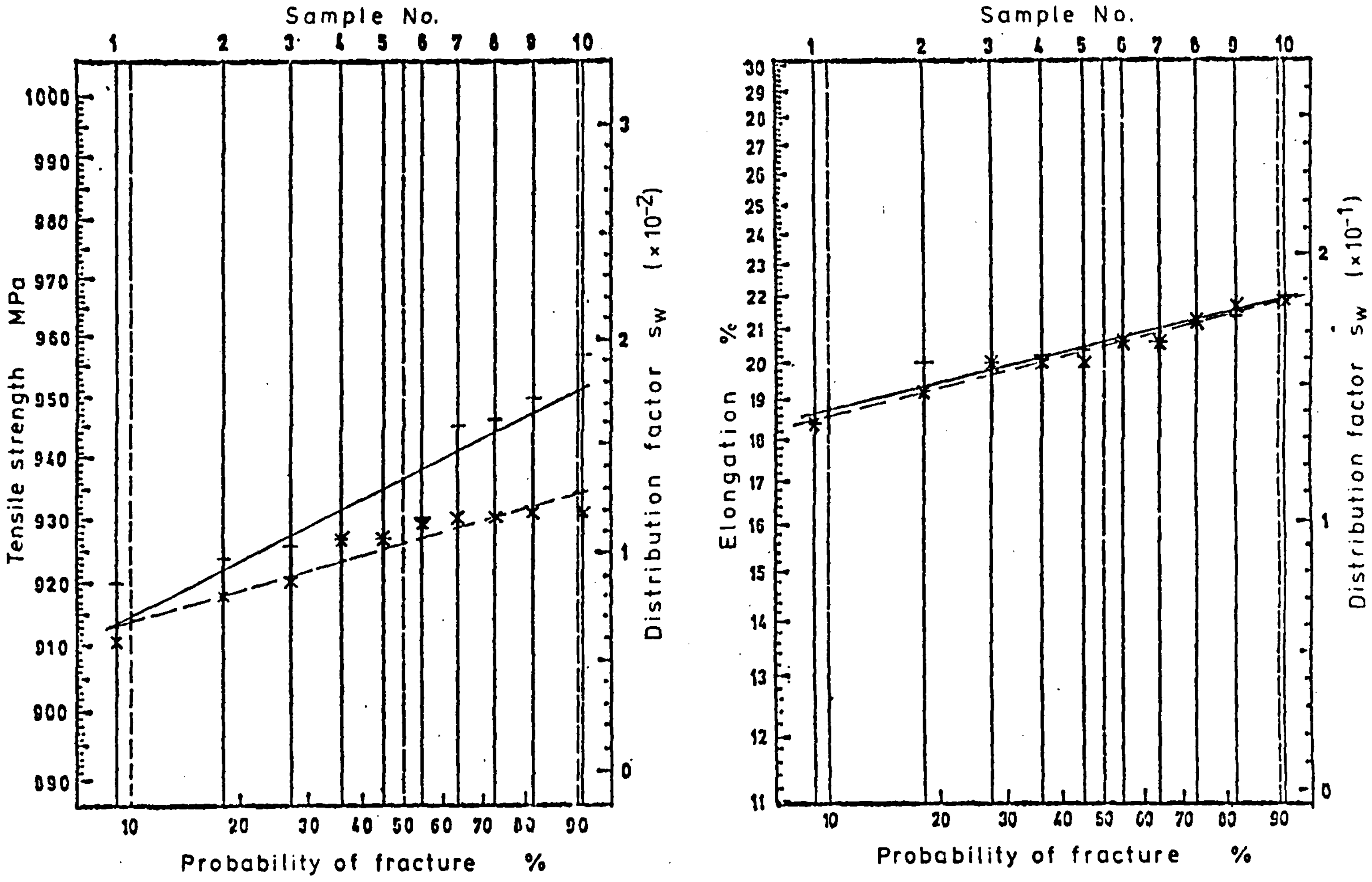
Table 18: Mechanical properties of the samples prepared from E24 and of the comparison samples from 503

		E 24				503			
ST °C	TP °C	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
1485	+ 5	17,0720	920	20,6	297	17,0724	930	21,6	295
		17,0628	927	21,4	287	17,0569	918	19,2	292
		17,0926	930	20,0	290	17,0707	931	21,8	289
		17,0633	924	22,0	290	17,0764	920	20,0	294
1485	+ 3	17,0491	945	18,4	286	17,0589	929	20,6	291
		17,0670	946	20,2	284	17,0482	931	20,6	284
		17,0574	950	21,2	292	17,0812	911	18,4	287
1485	+ 1	17,0805	926	20,0	293	17,0380	927	21,2	292
		17,0686	927	20,6	292	17,0498	930	20,0	295
		17,0834	957	20,4	293	17,0556	927	20,0	295

Mean values ± standard deviations

	ρ_{Gr} g/cm^3	ρ g/cm^3	SS %	H_V	σ_{50} MPa	s_σ $.10^{-2}$	δ_{50} %	s_δ $.10^{-2}$
E 24	11,45 ± 0,01	17,07 ± 0,01	32,9	290 ± 4	937	1,255	20,6	4,875
503	11,70 ± 0,01	17,06 ± 0,01	31,4	291 ± 4	926	0,699	20,5	5,145

Fig.35: Weibull Diagrams for powder E24



solid line and - for powder E24

broken line and x for standard powder W503

Powder E27 (100 ppm U)

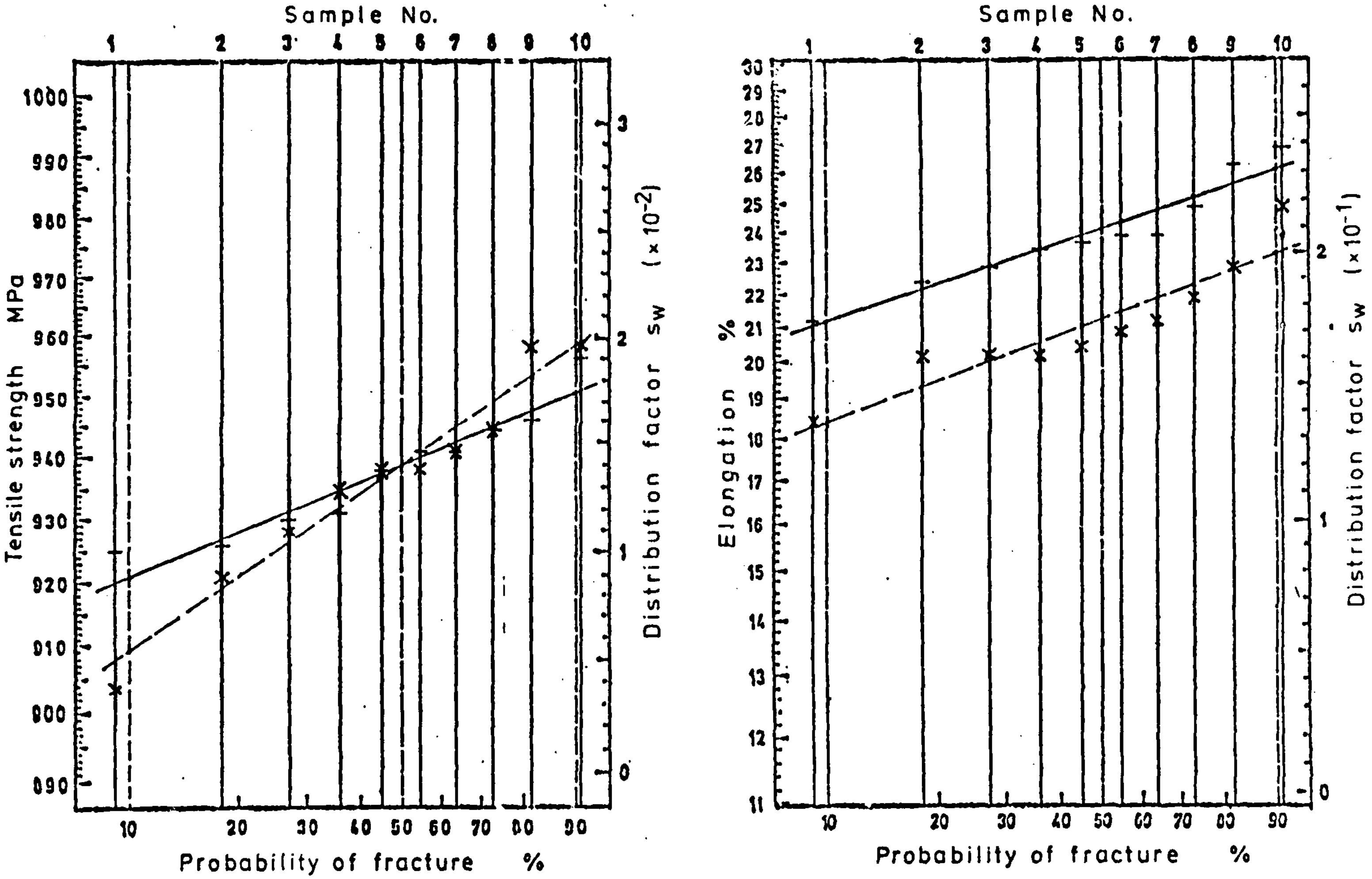
Table 19: Mechanical properties of the samples prepared from E27 and of the comparison samples from 5O3

		E 27				5o3			
ST °C	TP °C	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
1475	+ 6	17,1o1o	925	26,2	3o2	17,o721	9o4	21,2	295
		17,o923	931	26,8	3o2	17,o855	928	24,8	292
		17,o795	946	23,8	292	17,o8o2	94o	2o,8	295
		17,o748	956	23,8	298	17,o949	944	22,8	292
147o	+ 5	17,o855	941	23,4	3o2	17,o715	958	18,4	292
		17,o7o2	938	22,4	294	17,o796	958	2o,2	295
147o	+ 3	17,o722	926	23,6	295	17,o796	921	2o,2	293
		17,o993	944	21,2	3o1	17,o861	935	2o,4	294
		17,o725	93o	22,8	296	17,o898	938	21,8	294
		17,o745	841	24,8	294	17,o834	938	2o,2	298

Mean values ± standard deviations

	ρ_{Gr} g/cm^3	ρ g/cm^3	SS %	H_V	σ_{5o} MPa	s_σ $.1o^{-2}$	δ_{5o} %	s_δ $.1o^{-2}$
E 27	11,82 ± o,o4	17,o8 ± o,o1	3o,8	298 ± 4	939	o,998	24,o	6,737
5o3	11,7o ± o,o1	17,o8 ± o,o1	31,5	296 ± 5	938	1,699	21,2	7,412

Fig.36: Weibull Diagrams for powder E27



solid line and - for powder E27
broken line and x for standard powder W503

Powder E30 (188 ppm Na, 113 ppm U, 106 ppm Al, 500 ppm F)

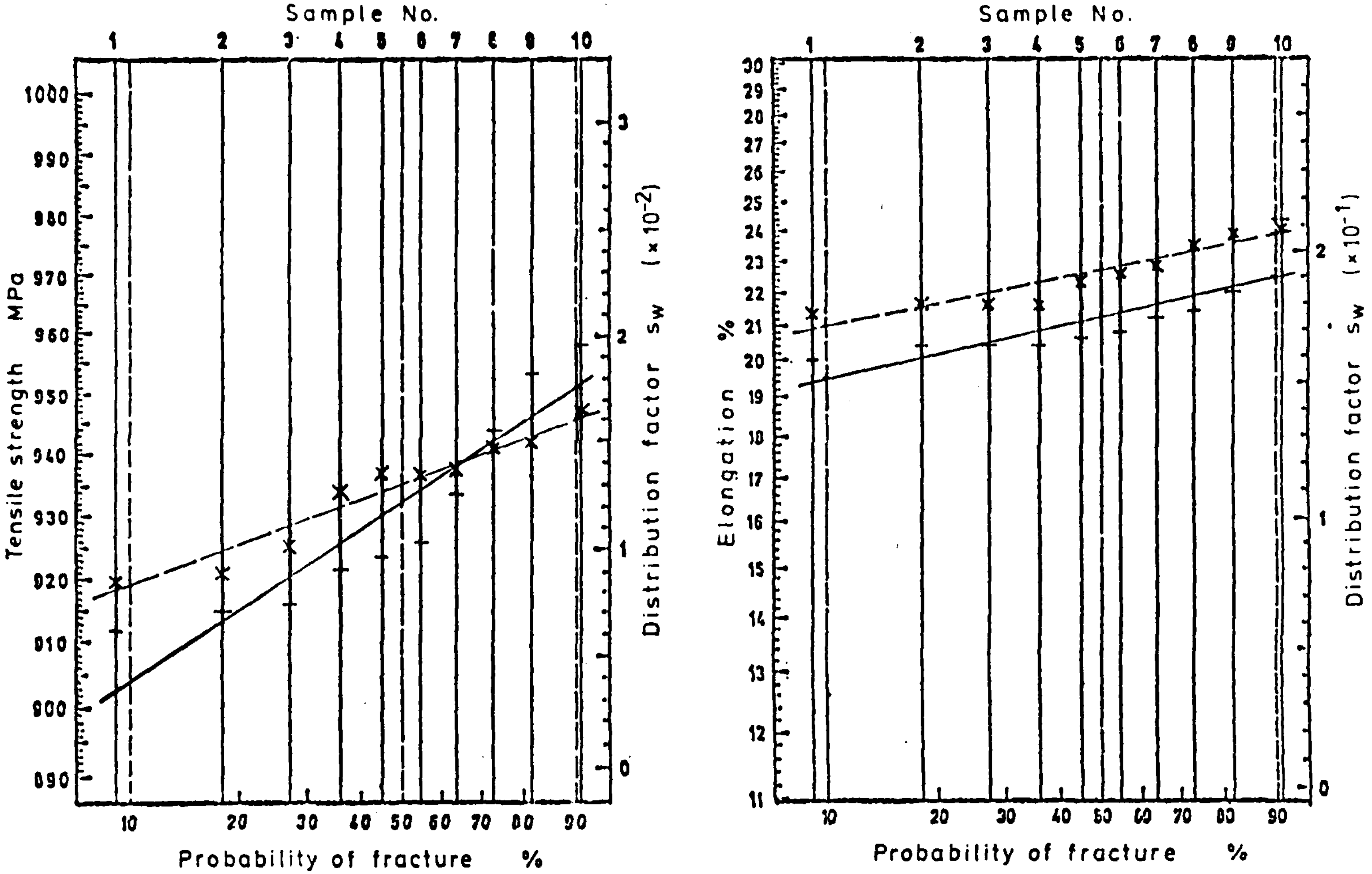
Table 20: Mechanical properties of the samples prepared from E30 and of the comparison samples from 503

		E 30				503			
ST °C	TP °C	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
1480	- 5	17,0374	927	20,0	300	17,0618	941	23,8	297
		17,0488	912	20,4	295	17,0625	920	22,4	290
		17,0428	915	20,4	295	17,0623	925	23,4	287
		17,0524	924	24,4	298	17,0200	921	21,6	293
1470	+ 3	17,0166	922	20,4	290	17,0404	947	21,6	306
		17,0293	916	21,2	293	17,0299	934	21,6	291
1490	0	17,0349	958	22,0	298	17,0491	937	22,6	295
		17,0337	953	21,4	292	17,0533	942	21,4	290
		17,0292	944	20,8	298	17,0430	938	22,8	290
		17,0385	934	20,6	299	17,0504	937	24,0	296

Mean values ± standard deviations

	ρ_{Gr} g/cm^3	ρ g/cm^3	SS %	H_V	σ_{50} MPa	s_σ $.10^{-2}$	δ_{50} %	s_δ $.10^{-2}$
E 30	11,86 ± 0,01	17,03 ± 0,01	30,4	295 ± 3	932	1,610	21,3	4,661
503	11,70 ± 0,01	17,05 ± 0,01	31,4	294 ± 6	935	0,956	22,6	4,001

Fig.37: Weibull-Diagrams for powder E30



solid line and - for powder E30

broken line and x for standard powder W503

Powder E33 (no doping additives)

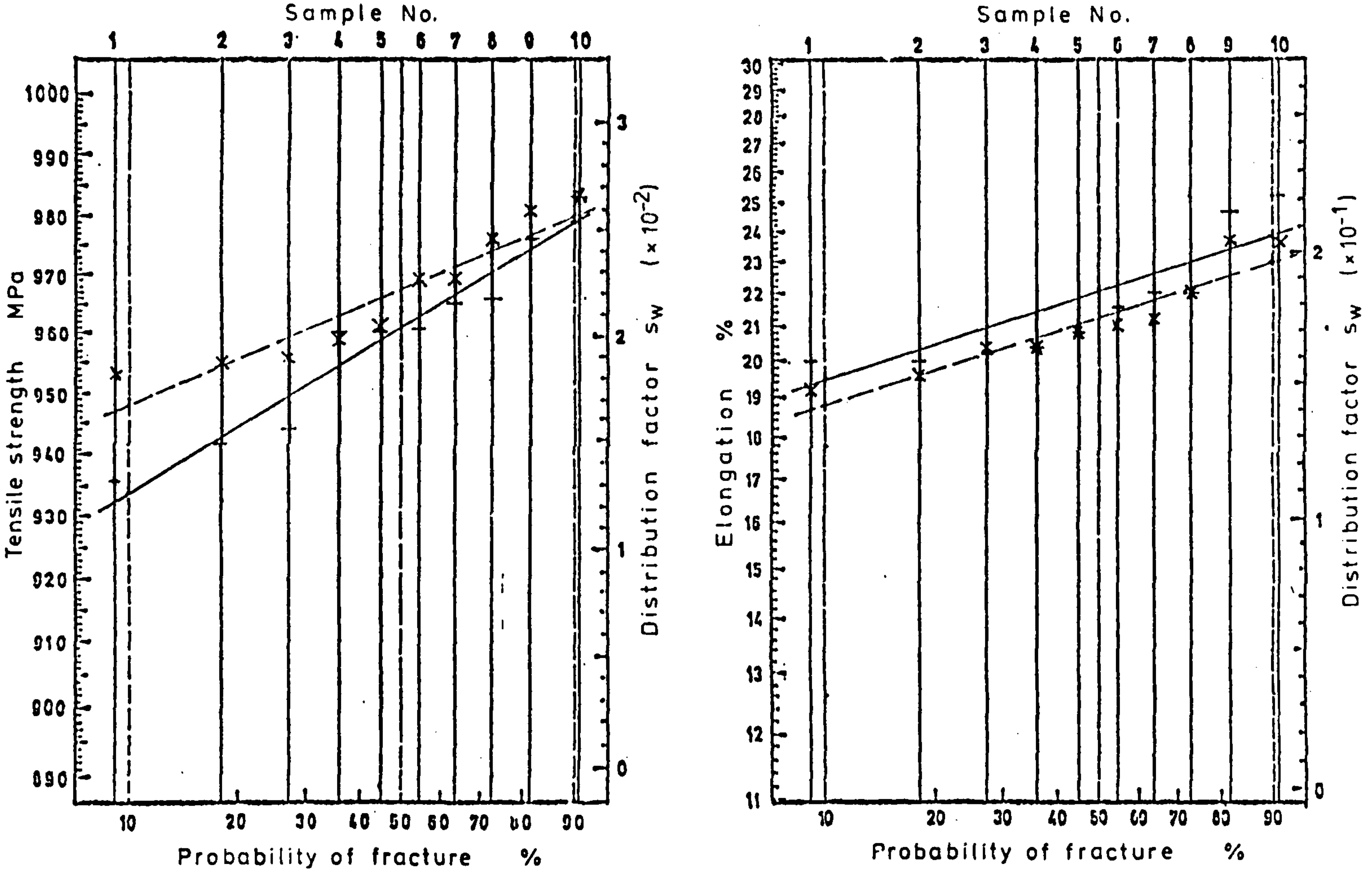
Table 21: Mechanical properties of the samples prepared from E33 and of the comparison samples from 503

		E 33				503			
ST °C	TP °C	ρ g/cm³	σ_B MPa	δ %	H_V	ρ g/cm³	σ_B MPa	δ %	H_V
1470	+ 4	17,0799	966	20,4	292	17,0930	983	19,2	291
		17,0637	960	21,6	297	17,0836	976	20,4	292
		17,0769	976	20,8	295	17,0758	981	20,8	291
		17,0765	983	20,0	290	17,0850	969	19,6	296
1480	+ 5	17,0688	961	22,0	295	17,0620	956	20,4	293
		17,0483	936	20,0	295	17,0694	955	21,0	296
		17,0599	944	24,6	298	17,0647	961	21,2	291
		17,0643	942	22,0	291	17,0836	953	22,0	296
1475	+ 3	17,0708	965	25,2	295	17,0813	969	23,6	297
		17,0798	960	20,2	297	17,0707	959	23,6	293

Mean values ± standard deviations

	ρ_{Gr} g/cm³	ρ g/cm³	SS %	H_V	σ_{50} MPa	s_{σ} $.10^{-2}$	δ_{50} %	s_{δ} $.10^{-2}$
E 33	11,87 ± 0,01	17,07 ± 0,01	30,5	294 ± 3	961	1,508	22,0	6,455
503	11,70 ± 0,01	17,08 ± 0,01	31,5	294 ± 2	966	1,073	21,3	6,547

Fig.38: Weibull Diagrams for powder E33



solid line and - for powder E33
broken line and x for standard powder W503

Powder E36 (100 ppm Na)

Table 22: Mechanical properties of nonporous samples prepared from E36 and of the comparison samples from 503

		E 36				503			
ST °C	TP °C	ρ g/cm³	σ_B MPa	δ %	H_V	ρ g/cm³	σ_B MPa	δ %	H_V
1485	- 2	17,0808	937	21,4	288	17,0652	951	19,8	287
		17,0580	942	21,6	282	17,0607	940	21,4	292
		17,0733	954	21,6	291	17,0635	951	22,0	288
		17,0707	941	23,6	287	17,0639	960	22,2	295
1485	- 2	17,0621	919	20,0	292	17,0539	935	19,8	287
		17,0664	929	23,6	292	17,0512	932	17,2	190
		17,0606	919	22,0	284	17,0593	939	22,8	290
		17,0743	918	23,0	290	17,0609	925	16,0	287

Mean values ± standard deviations

	ρ_{Gr} g/cm³	ρ g/cm³	SS %	H_V	σ_B MPa	δ %
E 36	11,80 ± 0,03	17,07 ± 0,01	30,9	287 ± 5	932 ± 13	22,1 ± 2,1
503	11,70 ± 0,01	17,06 ± 0,01	31,4	289 ± 3	941 ± 9	20,2 ± 2,3

Table 23: Mechanical properties of porous samples prepared from E36 and of the comparison samples from 5O3

	E 36				5o3			
ST TP °C °C	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
1495 - 4	16,16o6	8o3	8,o	284	17,o629	929	22,o	287
	15,1484	758	4,8	279	17,o5o2	917	23,o	285

Powder E39 (50 ppm Na)

Table 24: Mechanical properties of the samples prepared from E39 and of the comparison samples from 503

		E 39				5o3			
ST ^oC	TP ^oC	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
1480	- 2	16,9o37	884	1o,8	281	17,o412	953	22,4	295
		16,9293	916	14,o	283	17,o27o	955	2o,o	29o
		16,8o23	926	1o,8	278	17,o635	976	22,o	295
		16,7796	92o	11,2	284	17,o639	96o	22,2	3o3

Mean values ± standard deviations

	ρ_{Cr} g/cm^3	ρ g/cm^3	SS %	H_V	σ_B MPa	δ %
E 39	11,64 ± o,o3	16,85 ± o,o7	3o,9	281 ± 3	911 ± 19	11,7 ± 1,5
5o3	11,7o ± o,o1	17,o5 ± o,o2	31,4	296 ± 5	961 ± 1o	21,7 ± 1,1

Powder E45 (50 ppm Li)

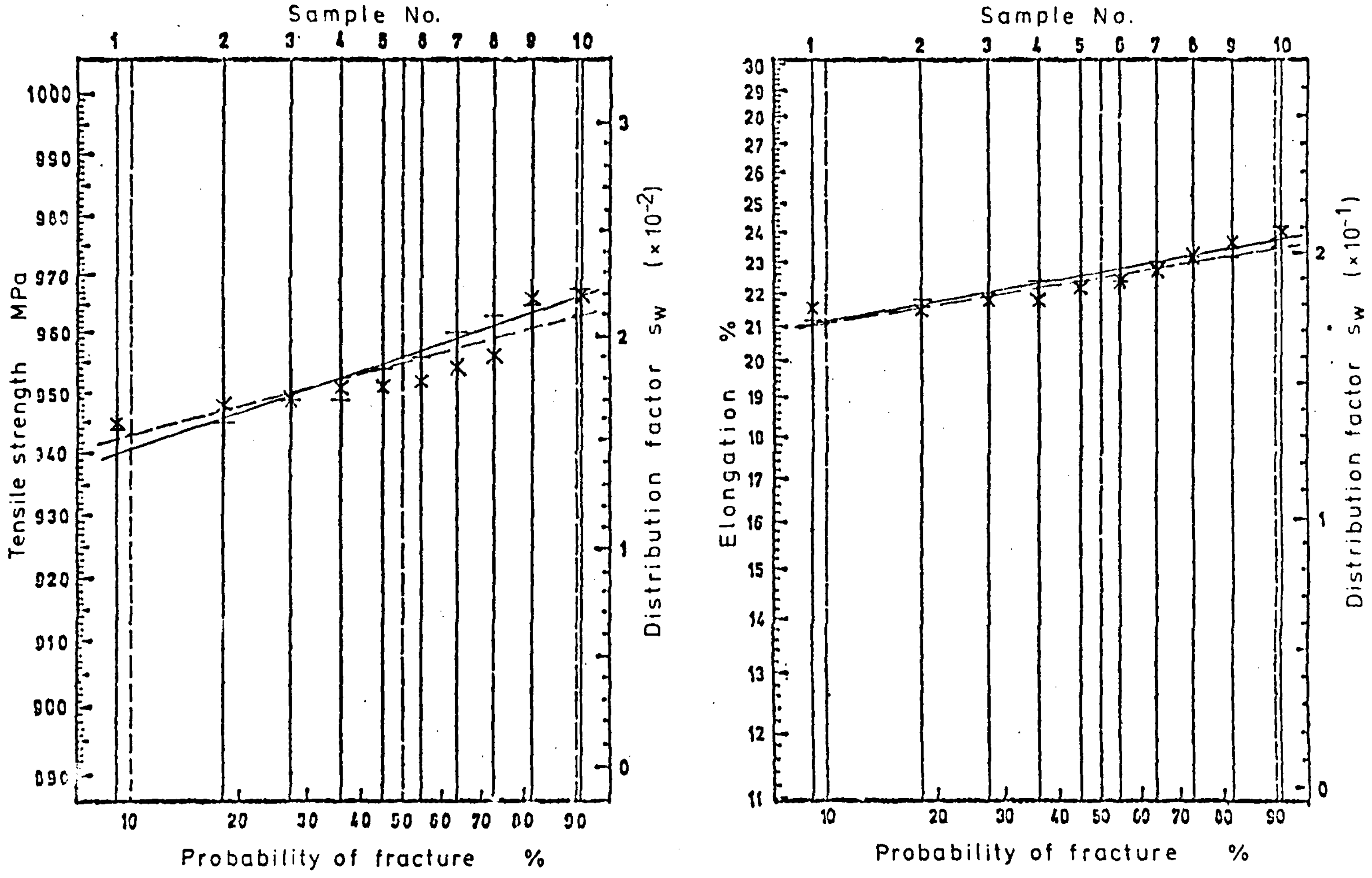
Table 25: Mechanical properties of the samples prepared from E45 and of the comparison samples from 503

		E 45				503			
ST °C	TP °C	ρ g/cm^3	σ_B MPa	δ %	H_V	ρ g/cm^3	σ_B MPa	δ %	H_V
1480	+ 3	17,0929	963	23,0	293	17,0333	951	23,6	290
		17,0855	944	22,4	297	17,0295	967	24,0	295
		17,0817	949	23,2	290	17,0433	966	22,4	292
		17,0456	965	22,4	288	17,0180	951	23,0	287
1485	+ 4	17,0801	968	22,4	286	17,0372	952	21,8	292
		17,1045	960	24,2	280	17,0451	949	21,6	282
1485	+ 3	17,1105	956	23,2	285	17,0466	954	21,6	286
		17,0918	945	21,8	290	17,0197	956	22,2	291
		17,0663	949	22,0	286	17,0183	945	21,8	296
		17,0669	954	21,2	287	17,0269	948	22,6	291

Mean values ± standard deviations

	ρ_{Gr} g/cm^3	ρ g/cm^3	SS %	H_V	σ_{50} MPa	s_σ $.10^{-2}$	δ_{50} %	s_δ $.10^{-2}$
E 45	11,98 ± 0,02	17,09 ± 0,02	29,9	288 ± 5	956	0,861	22,7	3,614
503	11,70 ± 0,01	17,03 ± 0,01	31,3	290 ± 4	955	0,681	22,5	3,398

Fig.39: Weibull Diagrams for powder E45



solid line and - for powder E45
broken line and x for standard powder W503

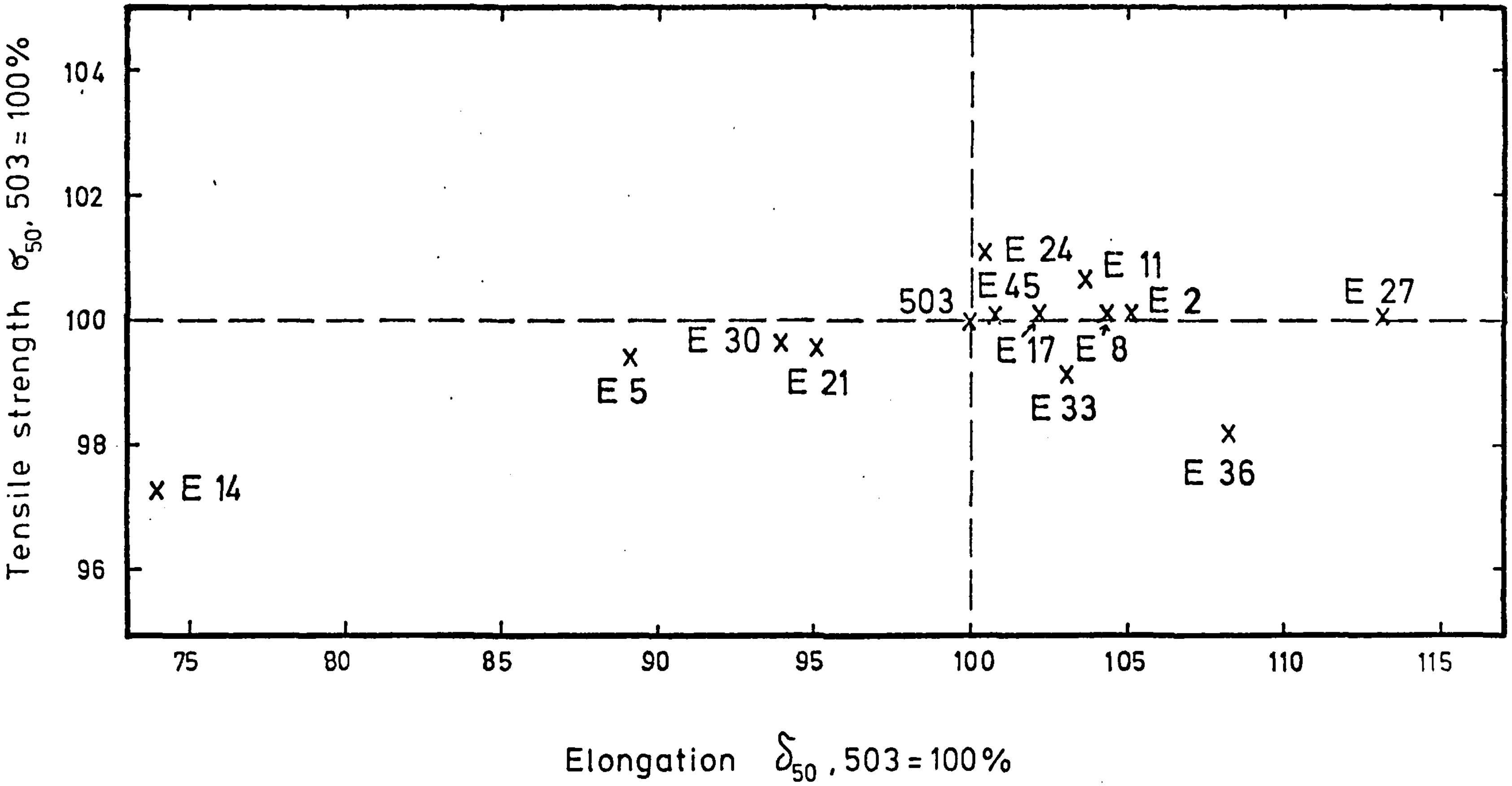


Fig.40: Comparison of σ_{50} and δ_{50} of all powders used

As is clearly shown by the tables and especially the Weibull-diagrams, all mechanical properties are excellently reproducible, even the elongations, which are very sensitive to even minor change in the sintering conditions. This becomes most evident when comparing the properties of standard samples prepared from W503/79 which were sintered in different test series; both the absolute values and the slope of the Weibull straight line are relatively constant, indicating a reproducibility of the results, even over a period of several months. The samples prepared from doped powders show a similarly narrow scatter for the individual values. Only the tensile strength scatter is in a few cases somewhat different, but no fixed trend is discernible. Against this background, the results of the experiments appear very reliable.

The difference in tensile strength and elongation between doped and standard samples are shown to advantage in Fig. Here σ_{50} (the stress which would cause 50% of the samples to break) and δ_{50} of the differently doped heavy metals are shown, σ_{50} and δ_{50} of the standard samples being taken as 100% and the deviations of σ_{50} and δ_{50} of doped samples from those of the standard are shown for all doped powders. This diagram shows clearly that most doped powders result in very much the same mechanical properties for the heavy metals as the standard powders. Only E27, containing 100 ppm U, causes a marked increase in elongation; maybe U forms chemical compounds with impurities thus removing embrittling elements from W, while on the other hand samples sintered from E14 (250 ppm Al) show considerable decreases in ductility; probably layers of Al_2O_3 on the surface of the W grains (see Fig. 6) inhibit wetting between grains and binder. The only really important influence was observed on samples prepared from E36 and E39 containing Na; the samples were extremely swollen and were interlaced with pore channels.With E36 some faultless samples could be prepared that could also be tested. From samples sintered from E39, however, no meaningful results could be attained because the high porosity of the samples caused not only low mechanical properties but also a very wide scatter in the individual values, which could be regarded as more or less random.

Metallographic sections were prepared from all the types of heavy metals investigated. The microhardness of the binder and the W-grains were measured by counting the grains on strips 0,6 mm long; on each section 9 strips were counted and the average was calculated. The values thus gained are only relative, but for comparison purposes very reliable because of the excellent reproducibility.

Neither microhardness nor mean grain size show a definite relationship to the mechanical properties. For the heavy metal, with U however there is a very good coincidence in that these heavy metals, which were most ductile of all, showed a very small grain size and also a high microhardness especially of the binder. This according to Holtz (8) is essential for obtaining good elongations. With other powder, however, such a relationship is not evident.

These experiments have shown that in general W heavy metals are not extremely sensitive to different qualities of W powders, with the exception of a few elements, which should be contained in very small quantities (e.g. Al) or as chemical compounds not volatile at sintering temperatures (Na). This seems to be confirmed by the results of the experiments with E30W; the powder contains much more Na than E36 and E39 but gives faultless samples, apparently due to the Na being bound as NaF. Both absolute values and reproducibility of the mechanical properties of heavy metals sintered from doped powders are quite comparable, and sometimes better, than those of the undoped standard samples.

Table 26: Microhardness and mean grain size of W heavy metals prepared from different W powders

W powder	Microhardness (20g boad) W grains	 binder	mean grain size (um)
E2	391	301	19,5
E5	404	331	21,3
E8	411	309	19,5
E11	411	329	20,7
E14	396	318	19,9
E17	421	363	22,2
E21	465	369	18,0
E24	401	357	19,3
E27	465	363	17,4
E30	411	319	17,0
E33	373	319	21,3
E36	424	314	19,0
E39	411	319	18,5
E45	422	341	20,8
503	392	336	19,8

SUMMARY :

The principal aim of this project, to gain improved knowledge about the influence of fabrication parameters and impurities in the raw materials on the properties of W heavy metals with a composition of 90 wt% W, 6,7 wt% Ni and 3,3 wt% Fe was reached in two steps. During the first year, thorough investigations into the influence of grain size and grain size distribution of the W powders on the compactibility of the W-Ni-Fe powder mixtures showed W powders of ~3 µm to be optimal. Compactibility was improved most by adding 1% camphor as a pressing lubricant. The sintering tests revealed that thorough pre-reduction of the green samples before sintering inhibited the extreme brittlemess that can appear when oxidized powders are used and led to excellent and very reproducible mechanical properties. Slow cooling in the furnace after sintering almost doubled the obtained elongation.

SEM photos clearly showed the fundamental difference between non-reduced and pre-reduced samples:
The non-reduced samples exhibited only intergranular fracture, the binder phase being torn away from the W grains quite easily. Pre-reduction treatment very much improved the interphase strength between W grains and binder. The fracture in these samples ran indisciminately through grains and binder, most being clear cases of transgranular fracture.

Evaluation of the sintering parameters showed that at a temperature of ~1470°C and a sintering time of 30 min the optimum combination of mechanical properties was obtained. As was shown by grain size investigations on metallographic samples, longer sintering times and, to a lesser degree, higher sintering temperature cause unwelcome grain growth. From a sintering series comprising W heavy metals with 95 and 97% W it was determined that with these compositions temperatures of at least 1490°C

for an optimal 30 min sintering time were necessary to obtain complete density. Sintering under these conditions resulted in elongations of 13% and 4% respectively as compared to a typical 24% with 90% specimens.

During the second year the investigations concentrated mainly on the influence of W powder chemistry on the properties of the heavy metals. A large series of experiments was carried out to show definitely the difference between the powders. The samples were sintered under the optimum sintering conditions, and in the individual batches samples prepared from standard W 503/79 powder were sintered in at least 3 batches, thus permitting a meaningful statistical evaluation. Besides the usual Gaussian statistics, Weibull statistics already well established in many fields of technology and suitable for fracture analyses were selected. As with heavy metals tensile strength and elongation are usually directly connected, both were evaluated in this way, and the Weibull statistics showed the excellent reproducibility achieved in these experiments. For the entire test series, the values of the standard samples sintered in different batches remained nearly constant and for both doped and standard samples the scatter of the individual values in the batches was very nearrow. With this foundation reliable conclusions about the effect of impurities in W were possible.

The comparison of the different powders revealed that most doped powders result in mechanical properties very similar to those of standard samples; U is somewhat advantageous, but Al lowers the elongation considerably. Only Na as Na_2O really causes detrimental effects, resulting in very porous samples with accordingly low tensile strength and elongation. Na in non volatile compounds, e.g. NaF, $Na_2O.SiO_2$, however seems to be harmless.

From these tests it can be concluded that heavy metals are not very sensitive to small amounts of impurities in the starting W powders if certain elements are removed or are contained as harmless compounds. The selection of W powders for the production of heavy metals, therefore, seems to be a not very critical step in production of these alloys as for as chemical purity and trace impurities are concerned. It is however important as for as other properties, as grain size, agglomerates or grain size distribution are concerned.

Investigations into the influence of small amounts of other metals added to the Ni-Fe-binder did not result in improvements of the properties. The samples doped with V were very swollen and porous and accordingly exhibited very low mechanical properties and also poor reproducibility. Although the reproducibility of the other series was quite comparable to that obtained with standard samples, in only a few cases were the absolute values of the standard samples reached.

Thorough evaluation of the individual steps of the sintering cycle made it clear that the bake out of the pressing lubricant is not critical as long as a certain rate of de-waxing is maintained. At too low a temperature, the camphor reacts with the metal powders and the resulting carbides embrittle the sintered samples. Because of its vital importance, the pre-reduction treatment was thoroughly investigated. The optimum temperature for pre-reduction is between 1000° and 1200°C; at lower temperatures, the reduction rate is too low, at higher temperatures, the pores close too rapidly and the H_2 cannot penetrate the bars to reduce them completely. Tests with pre-oxidized samples confirmed the effectiveness of the pre-reduction by raising the temperature from 500 to 1400°C over a period of 6 hrs. Even strongly oxidized samples showed excellent properties after the sintering cycle. Extremely slow cooling of the samples from sintering temperature to 1415°C did not result in improvements over samples conventionally cooled in the furnace.

Heat treatments which were performed in H_2 at various temperatures and with various cooling rates resulted in embrittlement of the samples cooled rapidly after sintering while the samples cooled slowly reached satisfactory properties; with heat treatment in N_2, however, the cooling rate was of no importance for the properties of the samples. This effect indicated that hydrogen embrittlement and not intermetallic phase precipitates in the binder is responsible for the brittleness of the rapidly cooled samples. Slow cooling removes the H_2 as a vacuum heat treatment. Sophisticated heat treatments after sintering therefore are not essential; apparently the same effect can be achieved by cooling the samples slowly after sintering.

As final result of this work it can be stated that the influence of the sintering parameters is much more pronounced than that of the purity of the starting W powders, if they are in the normal range of a good high quality industrial product. For both absolute values and reproducibility of the mechanical properties, deviations from the optimum sintering cycle can do more harm than impurities in the W-powders. During production, therefore, control of the sintering process seems to pay off more than the purchase of extremely pure, and expensive, W powder.

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PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 5 W

DATE 79-04-30

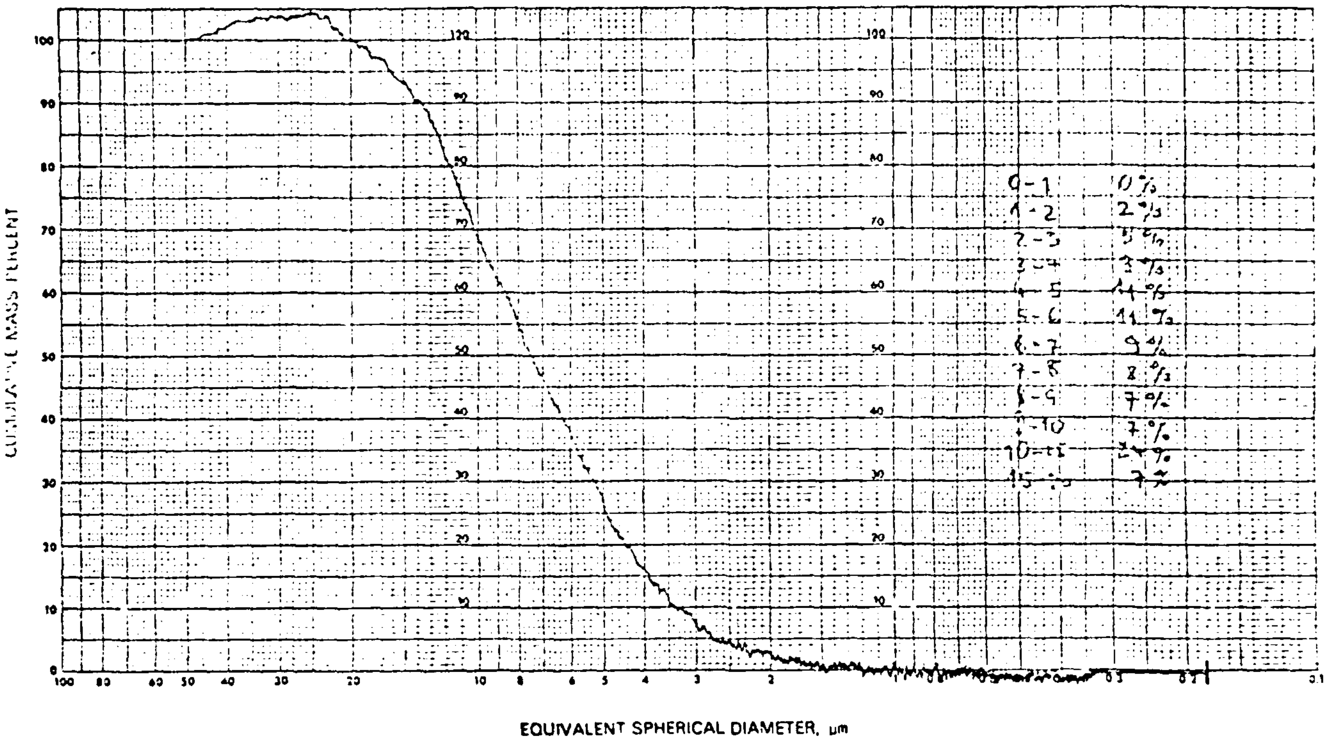
Density 19,3 g/cc LIQUID Sedisperse A-11 Density ______ g/cc Viscosity ______ cp

BY Pu

Preparation 60' deagglomeriert + 15' US

TEMPERATURE 28 °C

RATE 579 START DIA 50 μm



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1-2	2%
2-3	5%
3-4	3%
4-5	14%
5-6	11%
6-7	9%
7-8	8%
8-9	7%
9-10	7%
10-15	24%
15-20	7%

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PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 2 W

DATE 79-05-02

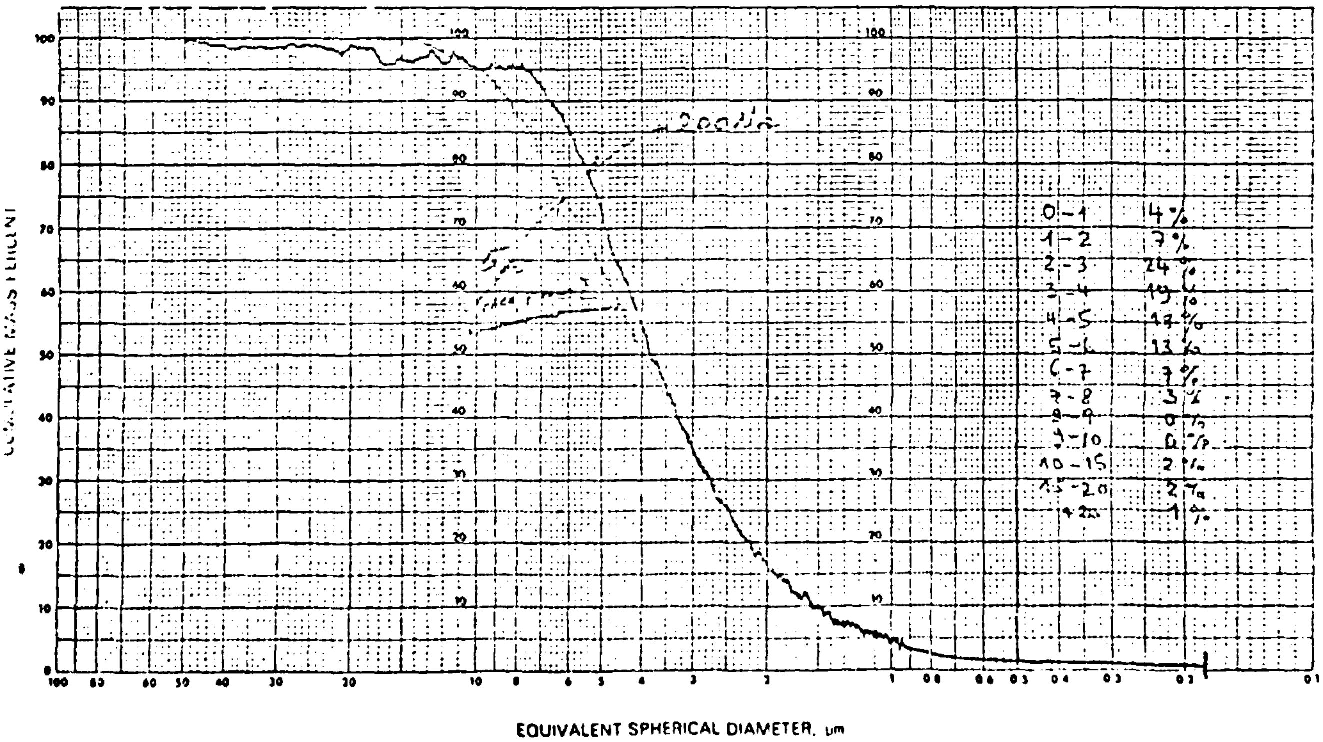
Density 19,3 g/cc LIQUID Sedisperse A-13 Density ______ g/cc Viscosity ______ cp

BY Pu

Preparation 60' deagglomeriert + 15' US

TEMPERATURE 27 °C

RATE 558 START DIA. 50 μm



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5-6	13%
6-7	7%
7-8	3%
8-9	0%
9-10	0%
10-15	2%
15-20	2%
>20	1%

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PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 11 W

DATE 79-05-02

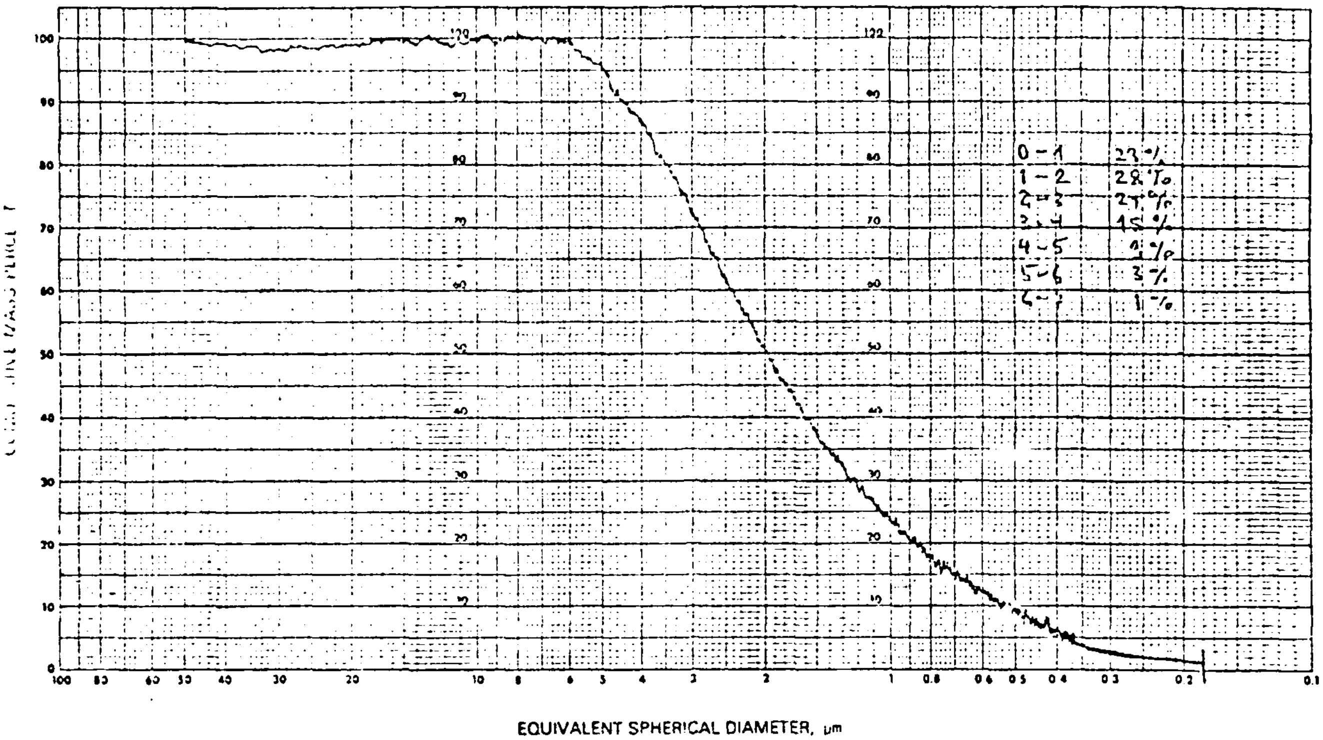
Density 19,3 g/cc LIQUID SEDISPERSE A-13 Density ____ g/cc Viscosity ____ cp

BY RA

Preparation 60' deagglomeriert + 15' US

TEMPERATURE 29 °C

RATE 597 START DIA 50 µm



0-1	23%
1-2	28%
2-3	21%
3-4	15%
4-5	9%
5-6	3%
6-7	1%

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PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 8 W

DATE 79-05-02

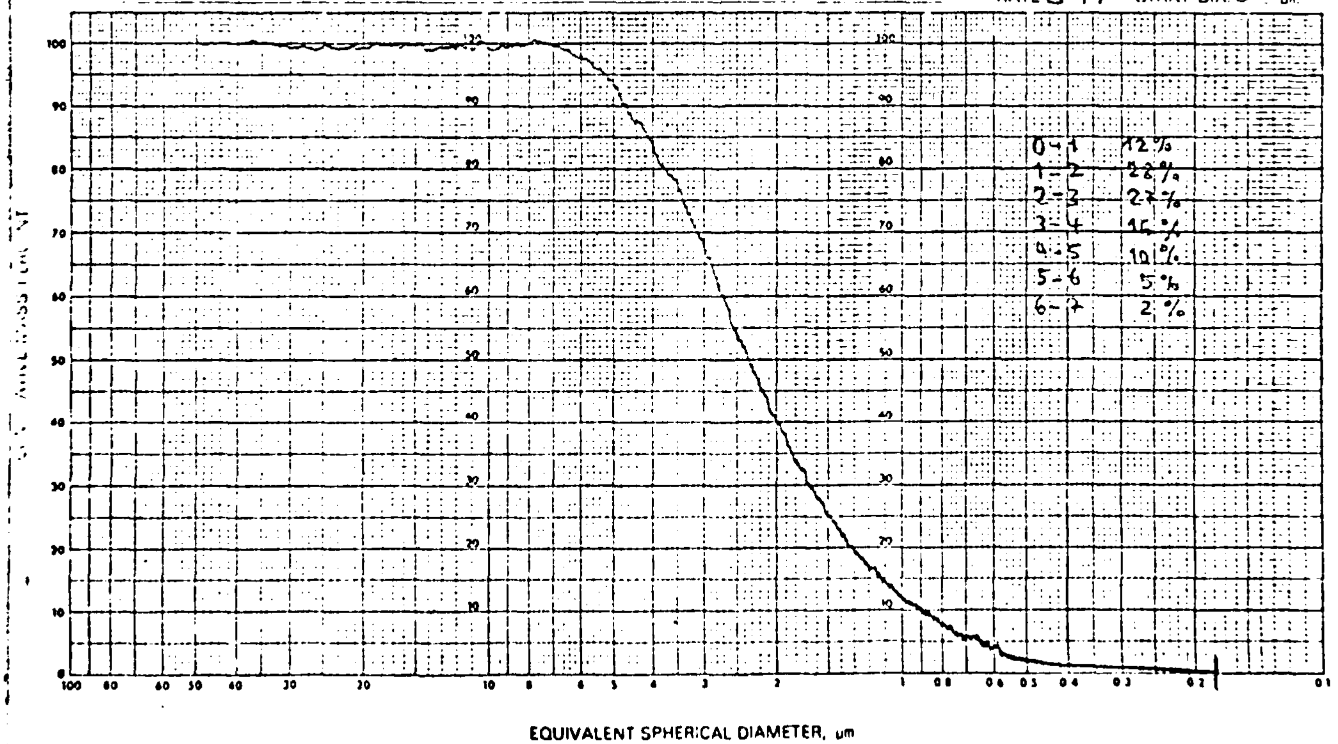
Density 19,3 g/cc LIQUID SEDISPERSE A-13 Density ____ g/cc Viscosity ____ cp

BY RA

Preparation 60' deagglomeriert + 15' US

TEMPERATURE 29 °C

RATE 597 START DIA 50 µm



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3-4	15%
4-5	10%
5-6	5%
6-7	2%

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PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 14 W

DATE 79-05-02

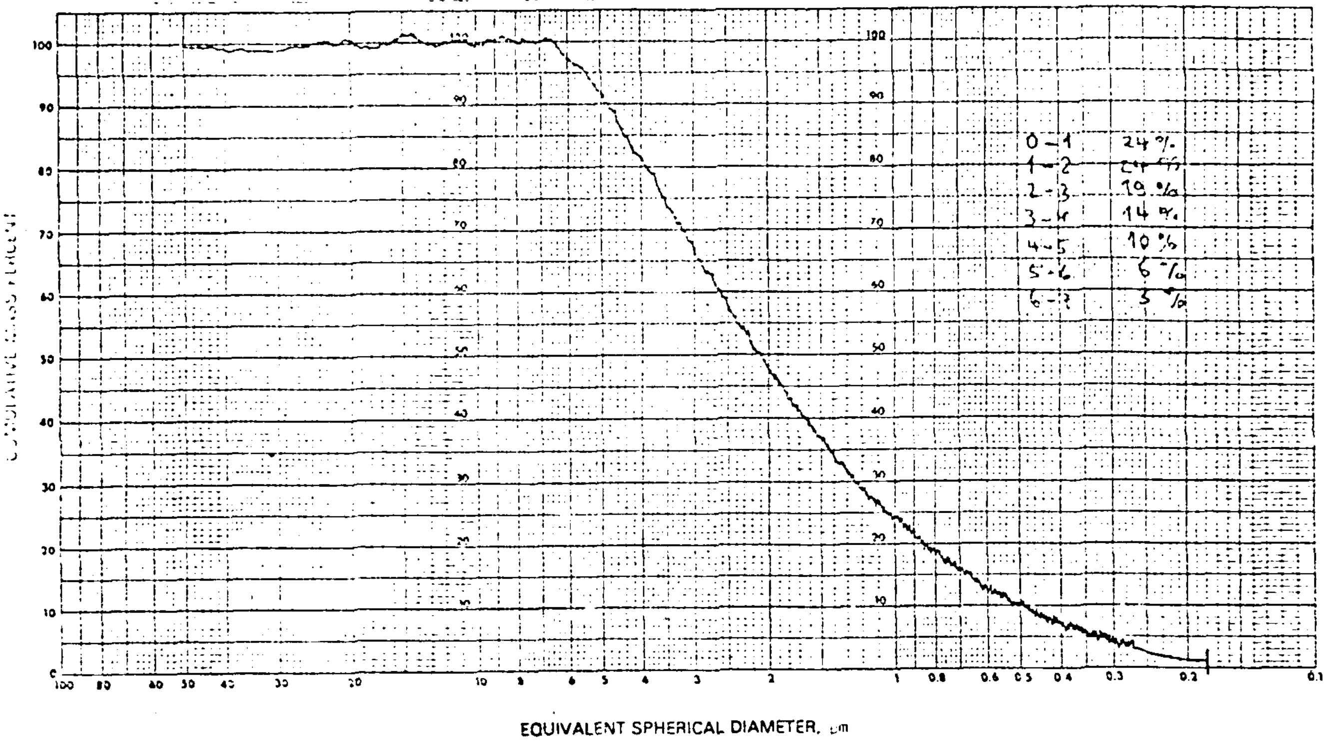
Density 19,3 g/cc LIQUID Sedisperse A-13 Density ____ g/cc Viscosity ____ cp

BY RA

Preparation 60' deagglomeriert + 15' US

TEMPERATURE 30 °C

RATE 616 START DIA. 50 µm



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1 – 2	24 %
2 - 3	19 %
3 - 4	14 %
4 - 5	10 %
5 - 6	6 %
6 - 7	3 %

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PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 17 W

DATE 79-09-11

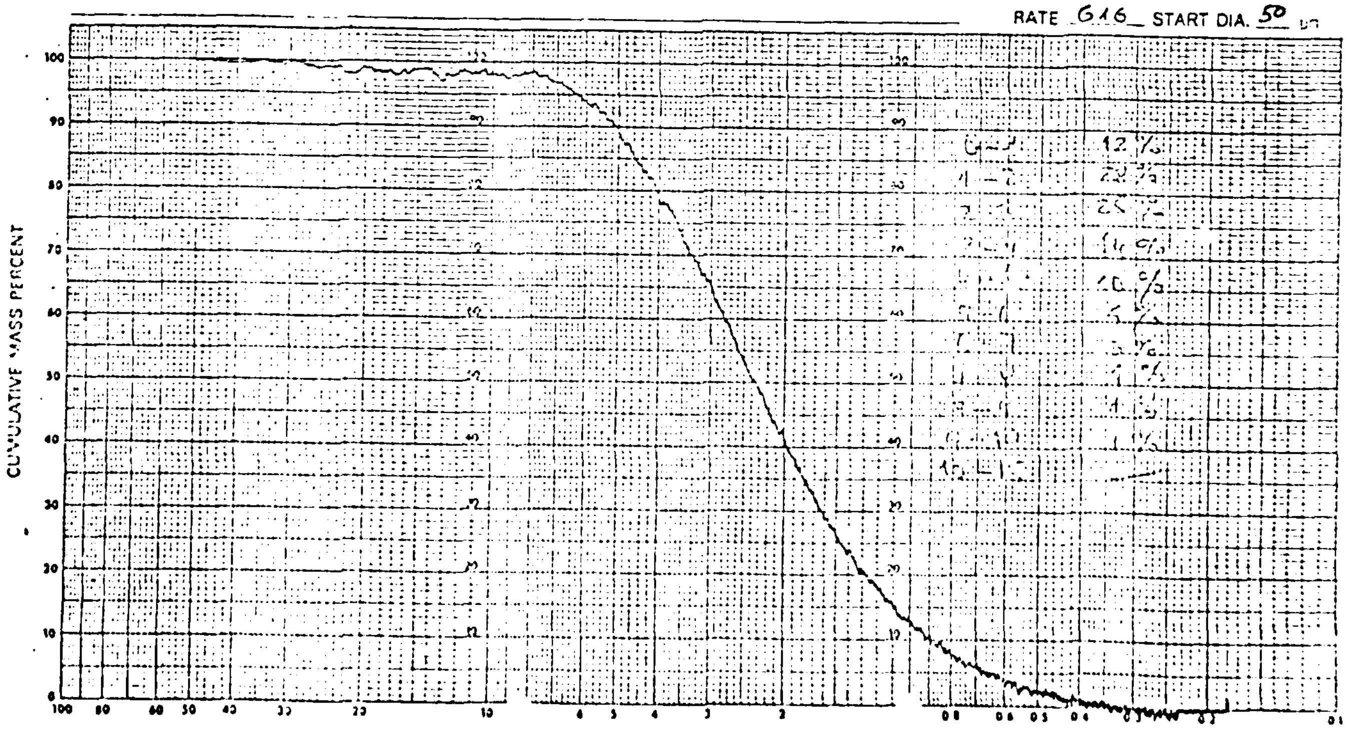
Density 19,3 g/cc LIQUID SEDISPERSE A-13 Density ____ g/cc Viscosity ____ cp

BY Koenig

Preparation 60' deagglomeriert + 15' US

TEMPERATURE 30 °C

RATE 616 START DIA. 50 µm



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1 – 2	22 %
2 – 3	25 %
3 – 4	14 %
4 – 5	10 %
5 – 6	5 %
6 – 7	3 %
7 – 8	1 %
8 – 9	1 %
9 – 10	1 %
10 – 15	–

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 24 W

DATE 79-09-11

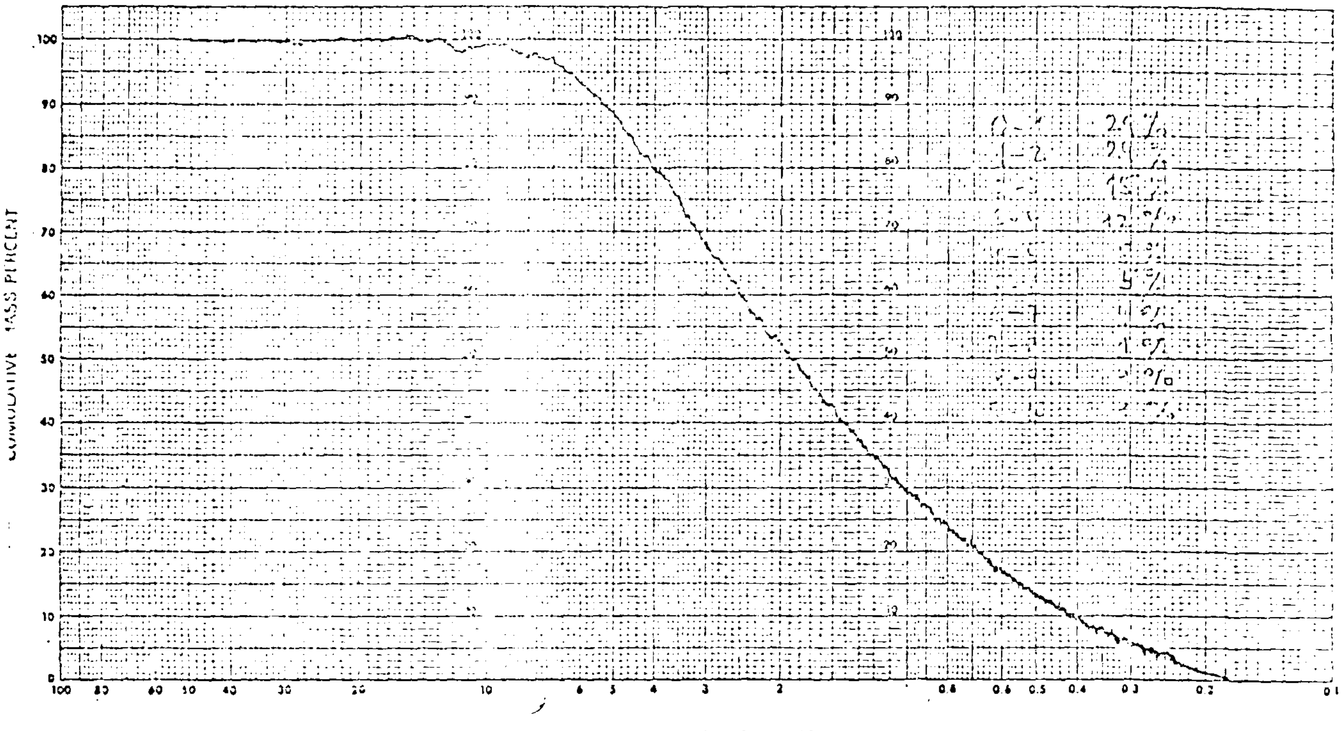
Density 19.3 g/cc LIQUID SEDISPERSE A-13 Density ____ g/cc Viscosity ____ cp

BY Koniazg

Preparation 60' deagglomeriert + 15' US

TEMPERATURE 33 °C

RATE 679 START DIA 50 µm



PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 21 W

DATE 79-09-11

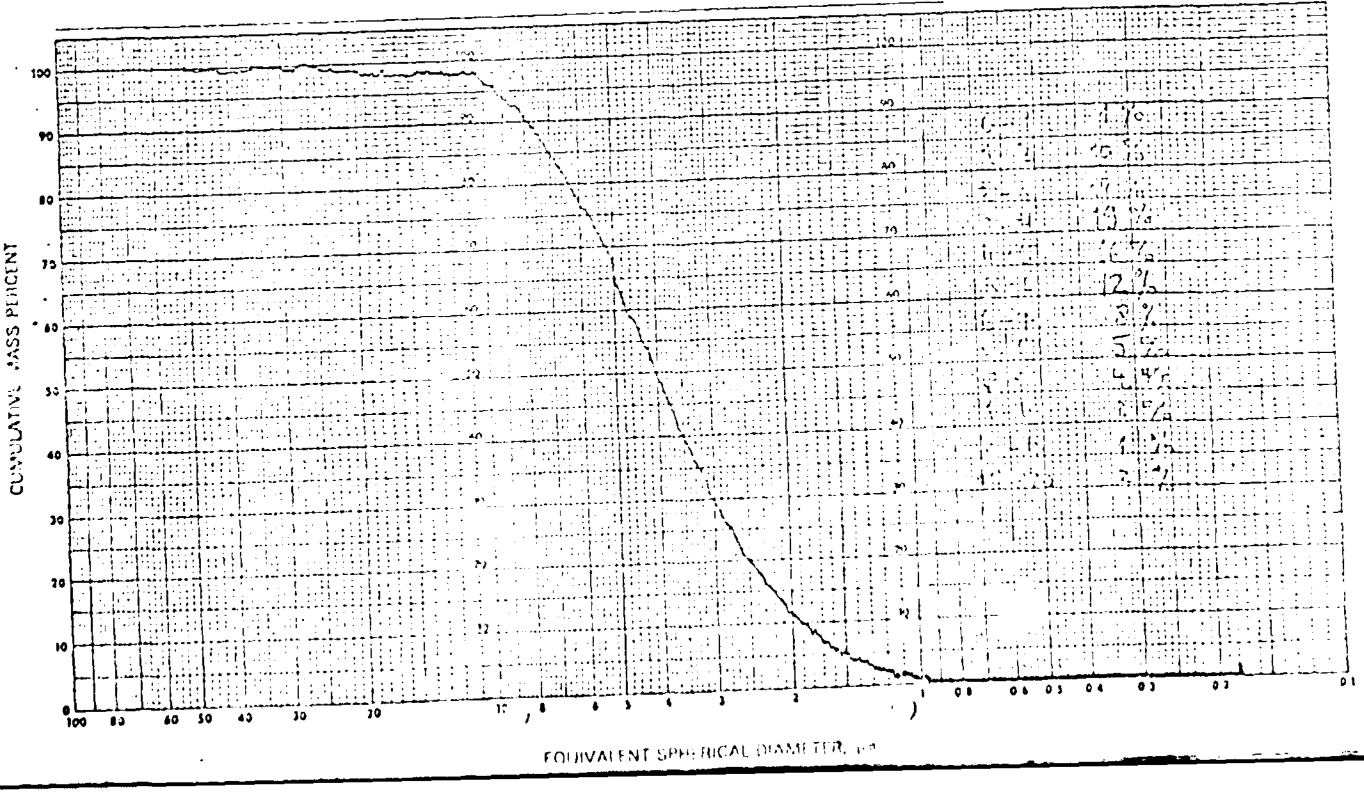
Density 19,3 g/cc LIQUID SEDISPERSE A-13 Density ____ g/cc Viscosity ____ cp

BY Koniazg

Preparation 60' deagglomeriert 15' US

TEMPERATURE 32 °C

RATE 659 START DIA. 50 µm



PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 30 W

DATE 79-04-30

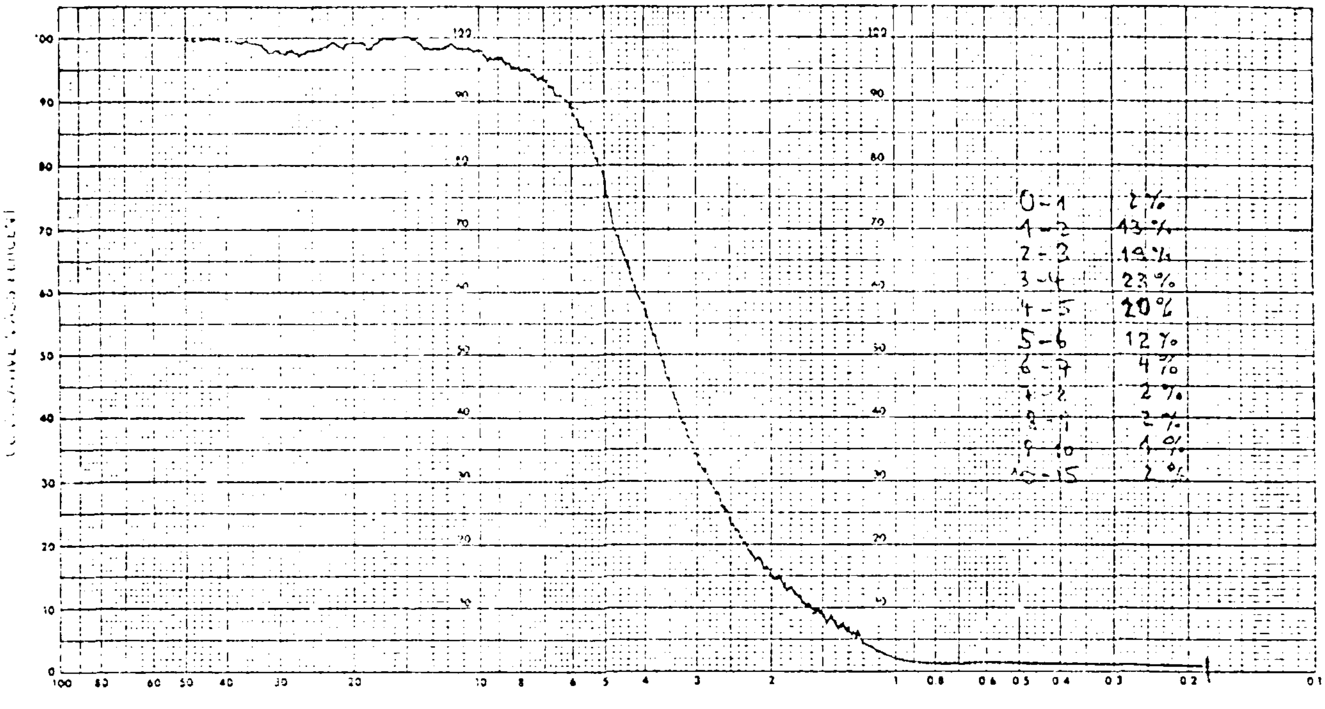
Density 19,3 g/cc LIQUID Sedisperse A-13 Density g/cc Viscosity cp

BY RA

Preparation 60' deagglomeriert + 15' US

TEMPERATURE 31 °C

RATE 657 START DIA 50 µm



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2-3	19%
3-4	23%
4-5	20%
5-6	12%
6-7	4%
7-8	2%
8-9	2%
9-10	1%
10-15	2%

EQUIVALENT SPHERICAL DIAMETER, µm

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PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 27 W

DATE 79-09-11

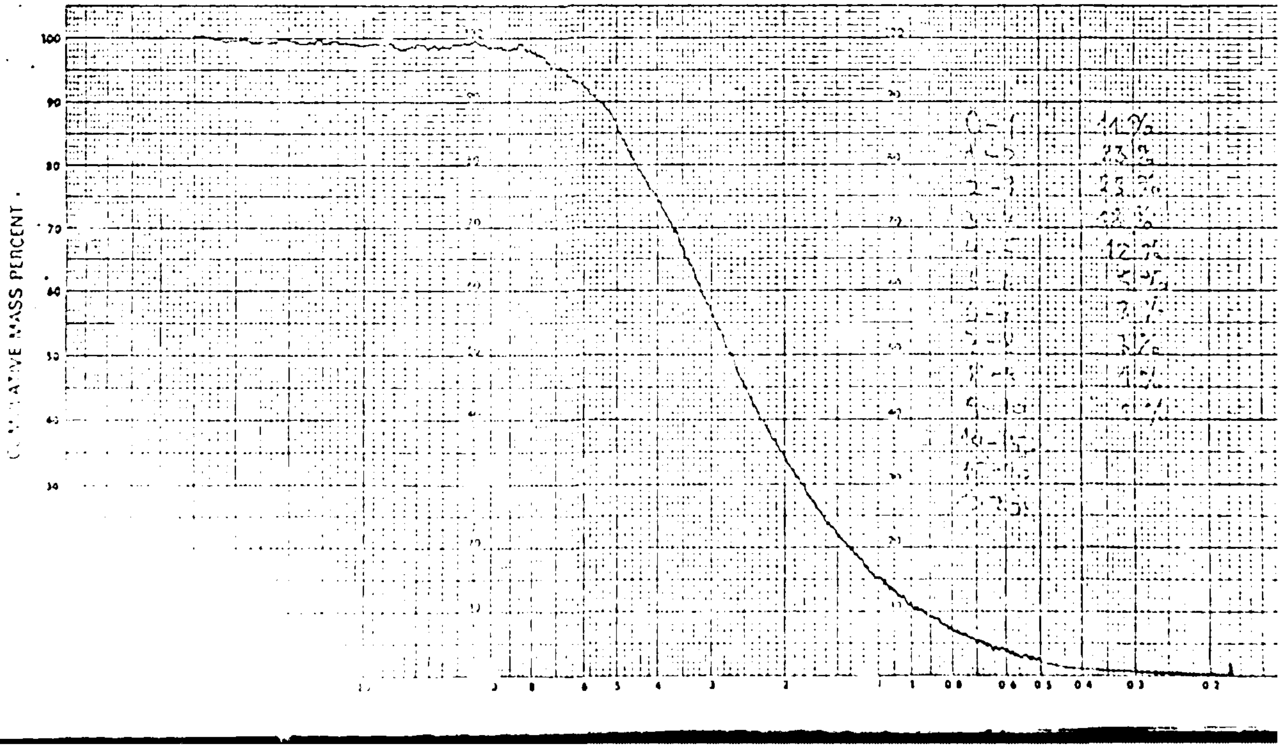
Density 19.3 g/cc LIQUID SEDISPERSE A-13 Density g/cc Viscosity cp

BY Kőnigg

Preparation 60' deagglomeriert + 15' US

TEMPERATURE 33 °C

RATE 679 START DIA 5



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3-4	22%
4-5	12%
5-6	5%
6-7	3%
7-8	3%
8-9	4%
9-10	[illegible]
10-12.5	
12.5-15	
15-25	

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 36 W

DATE 79-09-12

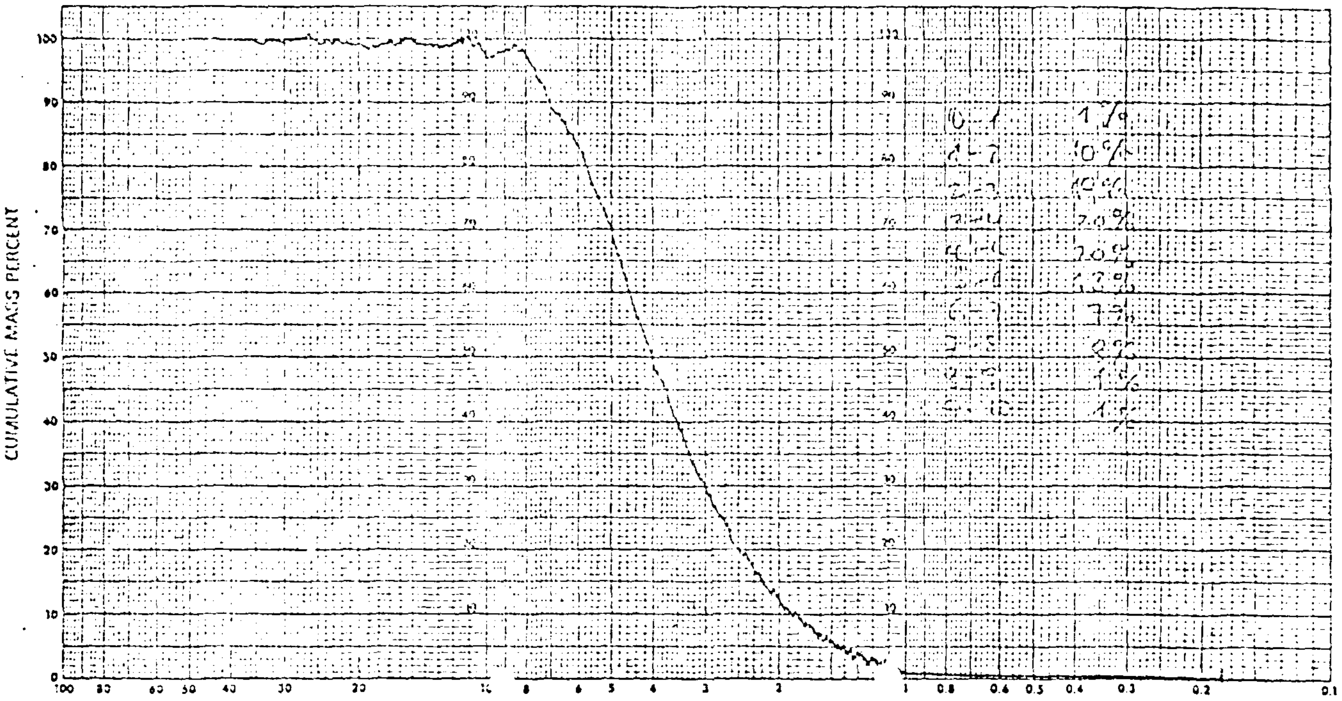
Density 19.3 g/cc LIQUID SEDISPERSE A-13 Density ______ g/cc Viscosity ______ cp

BY Kaiwyy

Preparation 60' deagglomeriert + 15' US

TEMPERATURE 28 °C

RATE 579 START DIA 50 µm



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3-4	20%
4-5	20%
5-6	13%
6-7	7%
7-8	2%
8-9	1%
9-10	1%

PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 33 W

DATE 79-04-30

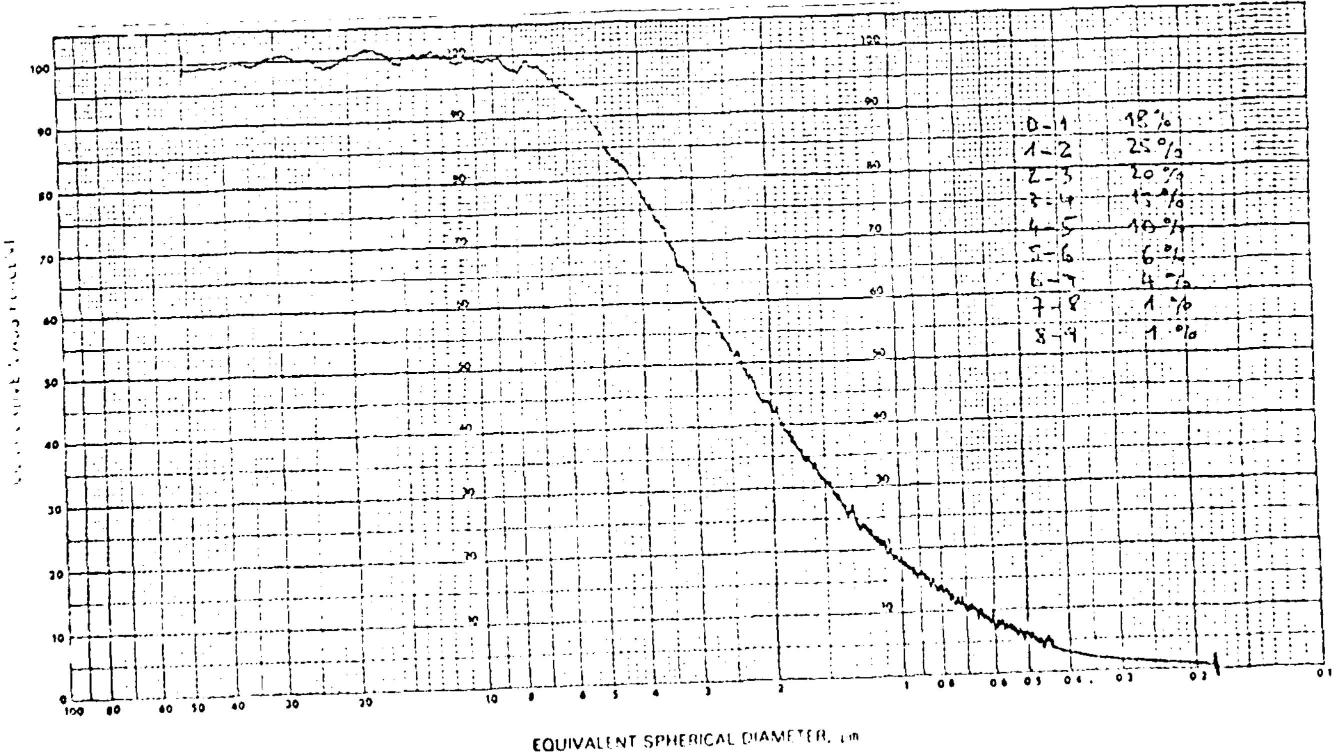
Density 14,3 g/cc LIQUID Sedisperse A-13 Density ______ g/cc Viscosity ______ cp

BY RA

Preparation 60' deagglomeriert + 15' US

TEMPERATURE 30 °C

RATE 616 START DIA. 50 µm



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5-6	6%
6-7	4%
7-8	1%
8-9	1%

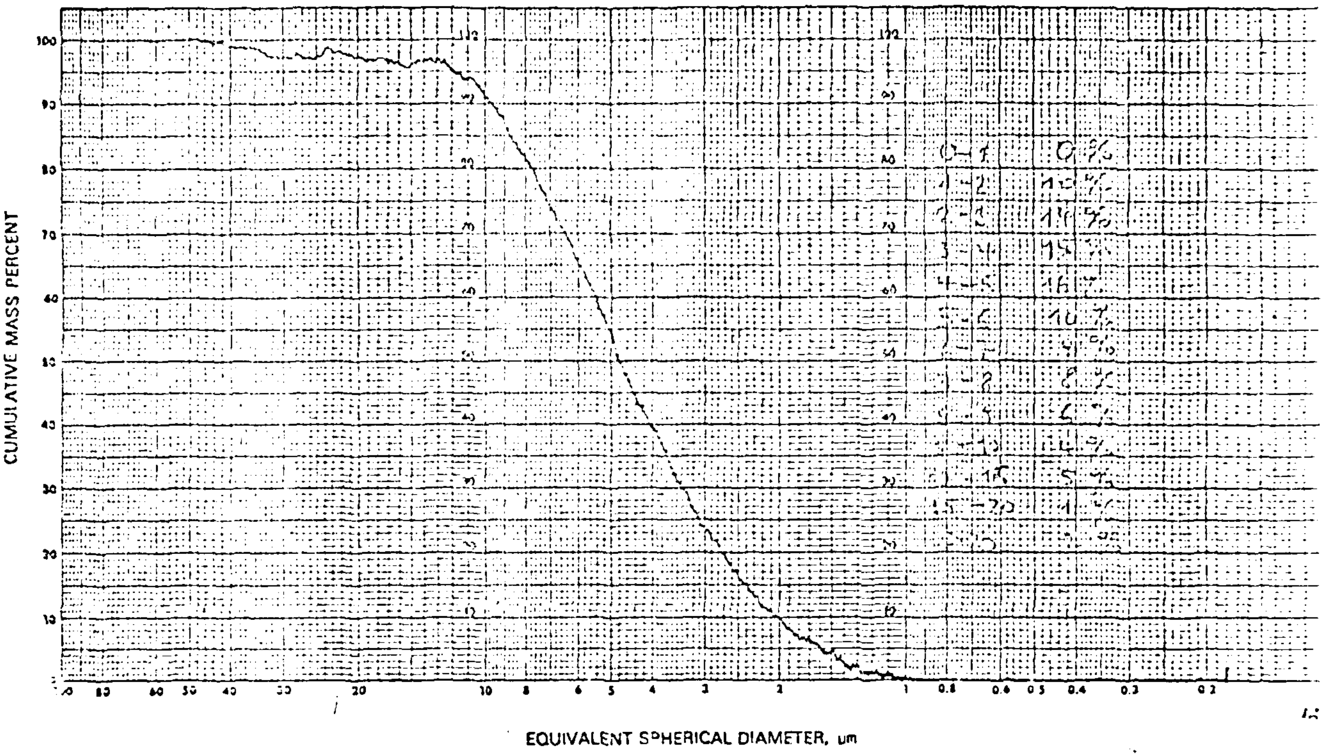
Density 19.3 g/cc LIQUID SEDISPERSE A-B Density ______ g/cc Viscosity ______ cp

Preparation 60' dwggl. + 15' US

BY Koniegg

TEMPERATURE 33 °C

RATE 679 START DIA. 50 µm



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PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION E 39 W

DATE 79-09-12

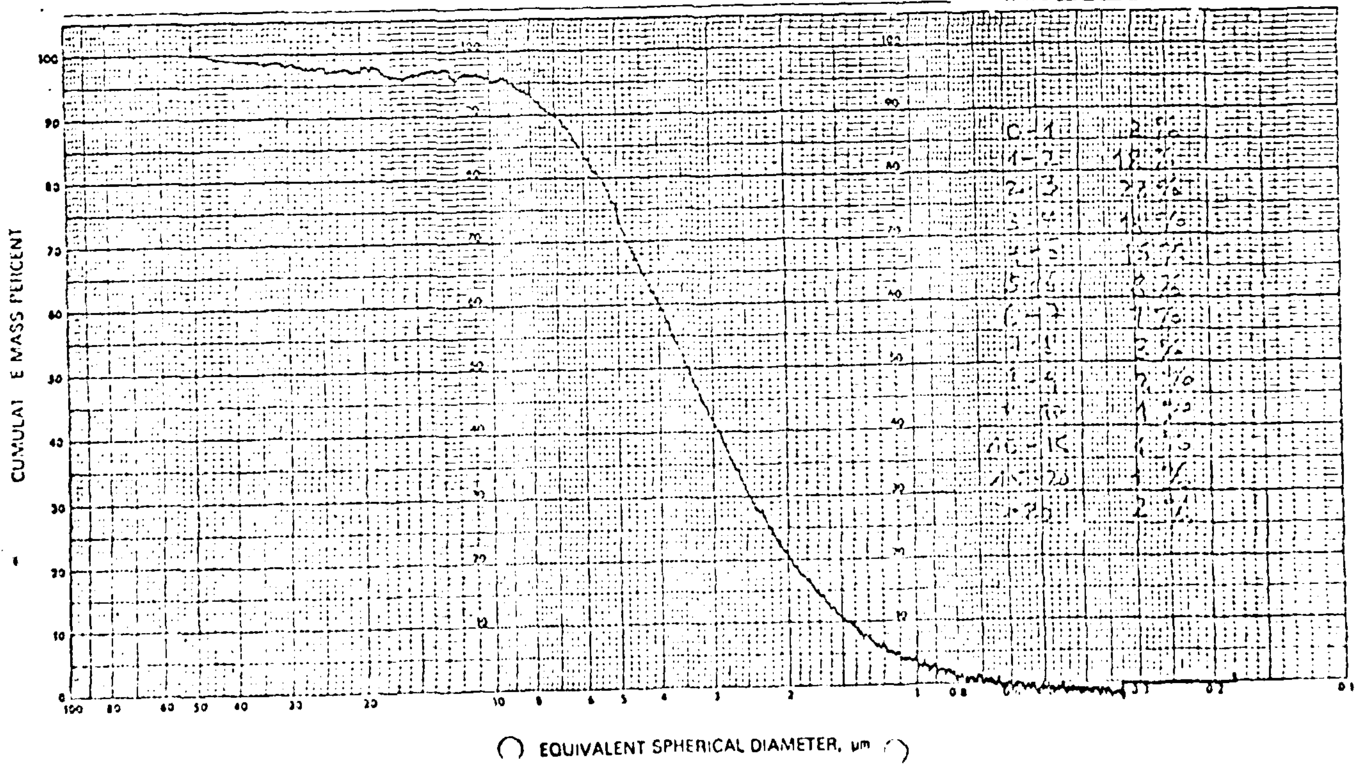
Density 19.3 g/cc LIQUID SEDISPERSE A-B Density ______ g/cc Viscosity ______ cp

BY Koniegg

Preparation 60' dwggl. + 15' US

TEMPERATURE 32 °C

RATE 659 START DIA. 50 µm



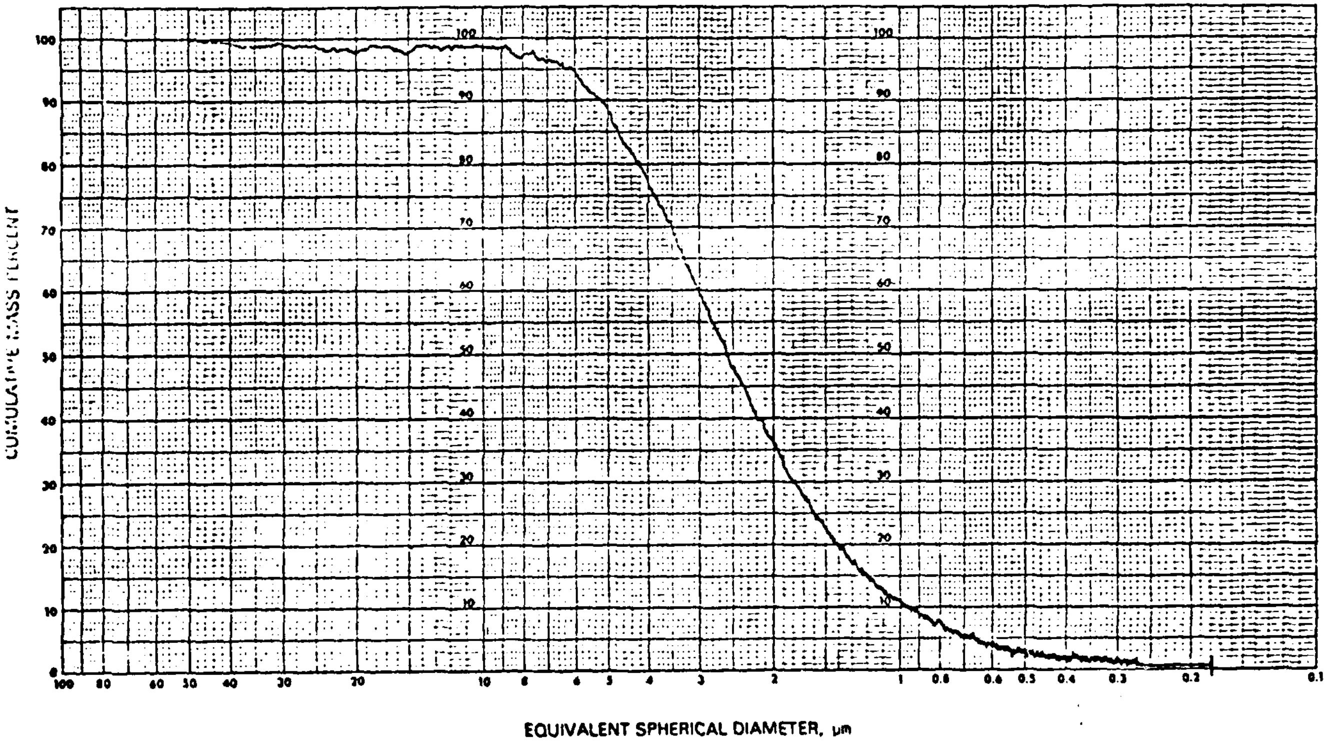
PARTICLE SIZE DISTRIBUTION

SAMPLE IDENTIFICATION 503 /79 WB D ( ) DATE 79-04-05

Density 19,3 g/cc LIQUID SEDISPERSE A-13 Density ___ g/cc Viscosity ___ cp BY RH

Preparation 60' deagglomeriert + 15' US TEMPERATURE 30 °C

RATE 59% START DIA. 50 µm



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