NASA TECHNICAL MEMORANDUM NASA TM-75745

FURTHER DEVELOPMENT AND APPLICATION OF POLYCRYSTALLINE METAL WHISKERS

Hermann J. Schladitz

(NASA-TM-75745) FURTHER DEVELOPMENT AND APPLICATION OF POLYCRYSTALLINE METAL WHISKERS (National Aeronautics and Space Administration) 61 p HC A04/MF A01 CSCL 11D

N80-26390

Unclas
G3/24 23598

Translation of: "Weiterentwicklung und Anwendung von polykristallinen Metallwhiskern," Bonn, Bundesmin. fuer Forsch. u. Technol. . Final Report, BMFT-FB-T-76-18, June 1976, 75 pp

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 DECEMBER 1979

STANDARD TITLE PAGE

1. Report No. NASA TM-75745	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle FURTHER DEVELOPMENT AND APPLICATION OF POLY-CRYSTALLINE METAL WHISKERS		5. Report Date December 1979
		6. Performing Organization Code
7. Author(s) Hermann J. Schladitz Physikalisch-Chemisches Forschungslabor, Munich (West Germany)		8. Performing Organization Report No.
		10. Work Unit No.
9. Performing Organization Name and Address .SCITRAN Box 5456 Santa Barbara, CA 93108		11. Contract or Grant No. NASW-3198
		13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code
15. Supplementary Notes Translation of: "Weiterentwicklung und Anwendung von polykristallinen Metallwhiskern," Bonn, Bundesmin. fuer Forsch. u. Technol. Final Report, BMFT-FB-T-76-18, June 1976, 75 pp. (N77-12219)		

16. Abstract

High-strength metal whiskers according to Schladitz (Z. Metallkunde, Vol. 59, 1968, No. 1, pp. 18-22) have a larger versatile field of application than monocrystalline whiskers. Although polycrystalline metal whiskers can be used for composites, preferably by extrusion in thermoplastics or by infiltration of resins or metals into whisker networks, the chief application at present may be the production and various use of whisker networks. Such networks can be produced up to high degrees of porosity and besides high mechanical strength, they have high inside surfaces and high electric conductivity. There are for instance applications concerning constructions of electrodes for batteries and fuel cells, catalysts and also new heat-exchanger material, being capable of preparing fuel oil and gasoline in order to assist a high-efficiency combustion. The technical application of polycrystalline metal whiskers required their modification as well as the construction of a pilot production unit.

17. Key Words (Selected by Author(s))		18. Distribution Statement Unclassified - Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 61	22.

NASA-HQ

Contents

/5*

*Numbers in margin indicate pagination in original foreign text.

Introduction into the properties of polycrystalline metal whiskers, also known and produced as so-called "Schladitz-whisker." /6

The metal whiskers whose development and application are the subject of this research report do not have the great scarcity value of monocrystalline whiskers which are also called hair or capillary crystals. Oxide whiskers and carbide whiskers cost thousands of DM (German marks) per kilogram, metal whiskers are completely out of reach.

The polycrystalline whiskers, especially iron whiskers, are relatively inexpensive high-strength hair-like metallic products and, of all whisker types, can be produced most cheaply and can be produced in a great number of modifications with regard to composition and properties. Their price is 50 DM per kilogram; this price could even be reduced because the end product, an iron compound, can be produced cheaply. They surely do not represent the final development of whiskers, but they make possible, in the near future, the utilization of numerous experiences and ideas which have resulted from the laborious and expensive whisker research, especially also research on monocrystalline whiskers.

The designation "whisker" at first was somewhat of a misnomer, for it was originally intended to characterize their particular hair-like shape, but the name whisker remained as a designation for monocrystalline hair-shaped products made from various materials and often having considerable specific strength.

The polycrystalline metal whiskers, the same as the monocrystalline ones, are the result of an accidental discovery which also was pursued with great interest. They are, as far as we can determine, a purely German development and only in recent times have they experienced strong interest in foreign countries, especially the USA; this is especially true because /7
of their very promising industrial application potential which is assigned an especially large space in the subject research report.

The polycrystalline metal whiskers are presently represented primarily by carbon-containing iron whiskers which are produced from iron-pentacarbonyl.

They are generated from originally extremely thin colloidal filament structures which, through further metal deposition, are quickly strengthened and thus grow from fibers of several Å in diameter to diameters in the micron range. In contrast to the monocrystalline iron whiskers the polycrystalline iron whiskers are made up of millions of extremely fine crystallites ranging in size from 70 to 90 Å. This build-up from submicroscopically small crystallites is partially the reason for the very high strength which, at times, was determined to be higher than 800 kp/mm^2, and not just as a single value. An additional contrast to the monocrystalline whiskers can be found in their unusually high number of mixtures (1.5×10^{12}). The largest number of the iron whiskers produced today in test quantities has strength values which are still far greater than those of carbon steels of the same composition.

As an aid in producing polycrystalline metal whiskers a strong magnetic field is used at the present time which keeps the very thin primary filaments in an erect position and protects them from destruction by gas molecules (see installation). Iron or nickel filaments of initial diameters of several hundred Angstrom can, by deposition of various metals in the gas phase, grow to diameters in the micron range so that, in this way, metal filaments of various compositions and also variable structure can be generated. Thus molybdenum, tungsten, and chromium filaments can be made from fine iron cores and nickel filaments with concentrically arranged layers of oxides, carbides can be made from alloys and similar combinations.

The production of polycrystalline metal whiskers is relatively simple, /8 and as already mentioned, inexpensive; its cost depends primarily on that of the metal combination. The production of 1 - 2 kg of whiskers per day has been carried out experimentally for years; in the near future production quantities of 50 kg of whiskers per day are envisioned as a basis of later production rates of tons per month.

Since the discovery of polycrystalline metal whiskers in 1935 our goal was to make them available for general industrial applications. The present report, among others, is intended to demonstrate the profitable application of whisker networks to actual problems such as environmental protection as well as point out savings in fuel as a first step in its valuable industrial application;

this could suggest new methods in fuel utilization, not only in Germany, but in the rest of the world.

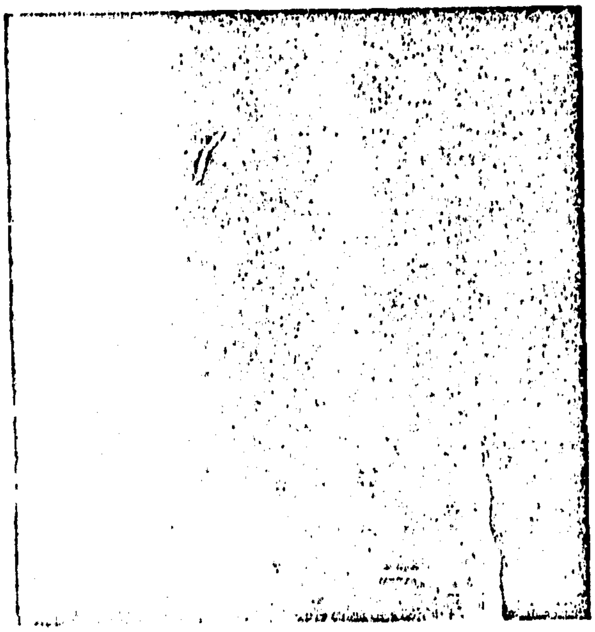


Figure 1

Program Section 1 /9

Optimal bonding of polycrystalline whisker to an optimal choice matrix to be reinforced

An obvious assumption for the bonding of a high-strength fiber to a matrix is the "purity" of the surface. In the case of polycrystalline metal whiskers this surface cleanliness is not always encountered since such whiskers, as used to be the case for monocrystalline iron whiskers, do not grow slowly in a hydrogen atmosphere, but develop at a very high rate of growth from a vaporized metallic compound with a complicated decomposition mechanism.

The polycrystalline iron whiskers which we investigated, generally have purposely generated thin oxide layer which protects them from the effects of the pyrophoric properties of these very fine specimens. In addition, surface impurities consisting of traces of adsorbed iron penta-carbonyl are present which, subsequently, can decompose without leaving loose iron oxide behind.

To remove the oxide from the iron whisker we have experimented with all the methods suggested in the literature without great success. The only practical method that remained was to reduce the whisker oxide layer in hydrogen which, however, for working temperatures above 300°C resulted in a reduction of fiber strength. An anodic etching of the whisker also appeared to be promising, but could only be carried out by us in small quantities.

Just as in galvanic precipitation of metals unto whiskers we carried out the anodic etching in a centrifuge developed for that purpose which was shaped so that the whiskers completely cover the leading centrifuge wall only during rotation while the opposite electrode contacts the developing ring of electrolyte in the centrifuge.

The centrifuge chamber, driven by a repulsion motor, is braked periodically
whereby the whiskers drop to the centrifuge bottom and then, as rotation of /10
the centrifuge is resumed, they will be freshly deposited on the wall.

It is this method of centrifuging, as already mentioned, which makes possible the galvanic precipitation of other metals unto iron whiskers such as nickel, copper, chromium and similar ones.

Since the oxide layer forms a very strong bond with the whisker, iron whiskers with such an oxide layer can be covered, in the gas phase, with nickel. Of course, the use of this method has to be restricted to special cases.

As already stated, polycrystalline metal whiskers grow through increases in the cross section of very fine primary filaments as the result of fast metal deposition. If high metal deposition rates are employed, one can achieve that the surface of the whisker, which is already quite coarse, becomes even rougher. This also is a method for increasing the bonding strength of whisker to matrix by increasing the contact area. Here it must be explained that the wartlike growths on the whisker surface do not represent a coarsening of the crystallites, but an accumulation of very fine crystallites which comprise the main material of the polycrystalline whiskers.

To bond the polycrystalline metal whisker to a matrix the procedure described in the following is also sensible and useful. It concerns the production of more or less porous whisker skeletons from a network-like metallic combination of metal whiskers. Such a network which can be made with reproducible pore volume, can be subjected to further treatment much more easily than loose whiskers. As an example, by flooding such a whisker network of iron whiskers with a /11
thermally decomposable metal compound all heated whiskers can be covered equally with metallic deposits which, as described above, is rather awkward for loose whiskers. Such a whisker skeleton, prepared on its inner surface, can be filled rather easily by infiltration with a resin matrix and even with a metallic matrix; in this way the initial shape of the whisker skeleton can be used to produce a desired shape of the ultimate composite body. As an example, this composite body can be in the shape of a plate.

It should be mentioned that, because of the simple magnetic orientation of magnetic polycrystalline whiskers, skeletons of varying porosity can be produced from parallel-oriented whiskers. We use such skeletons in order to infiltrate, immediately after the reduction of whisker oxide layers, magnesium into the skeleton; the magnesium thus also penetrates whisker interspaces in the micron range.

In order to achieve, at least, a uniform distribution of whiskers in a resin matrix, one can attach them also by means of an organic or inorganic adhesive in the form of a network. The adhesives which must be diluted are to be chosen so as to provide, at the same time, a sort of adhesion promoter for the resin. There are a number of adhesives which have been proven to give good adhesion to metals such as, cyano-acrylate, anaerobic adhesives with hardeners, epoxy resins and declared metal adhesives.

The whisker networks, insofar as they have been produced by sintering, suffer a considerable decrease in hardness when carbon-containing non-alloyed or non-dispersion-hardened whiskers are used.

The hardness and, although we cannot yet test it, the strength are again /12
increased by boron treatment. A typical cross-section of a boron-treated whisker is shown in figure 2.

Figure 2

The whisker purposely has a soft core, but its surface hardness increases appreciably by the boron treatment, up to 1600 kp/mm^2 and above. Iron boride layers have hardnesses of up to 2100 kp/mm^2. Since the iron boride layers are produced on the whiskers at temperatures between 900 - 1000^0 C, the whiskers can later on be used in the matrix up to those temperatures without losing their hardness. The method for effective boron treatment of loose whiskers and those attached to the skeleton as well as the suitability of the boron surface for combining it with different matrices has not yet been finalized.

Program section 2 /13

Improvement and adaptation of the whisker production process to the demands for fiber reinforcement of a matrix

The first type of a whisker machine according to Schladitz which produces polycrystalline iron whisksrs in kilogram quantities by decomposition of iron pentacarbonyl produces them inside of a given reaction volume of varying dimensions. As has already been mentioned at the beginning of this report, the shorter the periods in which the whiskers are produced and then ejected from the reaction volume in quantities of several million whiskers, the more uniform in diameter the whiskers will be. The lengths of the polycrystalline metal whiskers of about 1 - 3 mm has not been changed so far. The production of long polycrystalline metal whiskers in a reaction volume is also possible although the yield per unit time is reduced thereby and the undisturbed production of the whiskers generates problems.

The discontinuous generation of polycrystalline metal whiskers should be complemented by a continuous production of larger amounts.

To produce metal whiskers continuously several different constructions were utilized. It was finally found to be very advantageous to allow the metal whiskers to grow on a moving belt from which they were continuously stripped outside of the reaction chamber. In order to implement this production technique, a number of side problems had to be solved and the mechanism of the individual phases of whisker production had to be again investigated in test setups.

These individual phases are essentially the following: /14

1) The decomposition of the metallic compound in the free space with the production of seed filaments.

2) Continued growth of the so-called primary filaments to form cores for subsequent whisker production.

3) Strengthening of the primary filaments by continued deposition of metal.

The improved production methods, with consideration of the just mentioned basic phases of whisker production, were designed to achieve the following advantages that could be expected:

1) Potential for producing whiskers of approximately equal length.

2) A large L/D ratio should optimally prevail.

3) Achievement of an ideal fiber shape which cannot easily be affected by disturbances such as during separation in the crowded reaction chamber

of the discontinuous machine.

4) Simplified operating conditions for the production of alloyed, resp. dispersion-hardened whiskers.

5) Favorable method for mass production of polycrystalline metal whiskers.

These efforts were rewarded through the construction of a continuous whisker machine for the mass production of metal whiskers from iron, especially for the technical realization of a whisker heat exchangeras shown in program section 5.

In the mean time it was necessary, for all research efforts of this report which required the whisker dimensions to be defined, to classify still better the whiskers produced from raw materials in the discontinuous production method according to DRP / 224 934 (German patent).

Although the separation of whiskers into different sizes by screening of the originally hard products by means of sieve sizes 3 to 0.063 did produce fractions of varying sizes, this crude method unnecessarily broke up many brittle whiskers and produced unusable pieces of short length. /15

The air separation which we employed used a tangential stream of CO_2 in a glass container to stir up fine whisker particles which then were removed by gas stream (CO_2) into a tube with upward slope and finally, through a hose with a 180° bend, fell into a collection chamber with a glass frit bottom. The glass container with tangential gas inlet was kept in constant centrifugal motion with a frequency of 50 Hz.

The thus occurring separation of the whiskers was gentle and generally effective for the separation of coarse fractions, but could only handle small amounts in a time-consuming manner. Whiskers in the micron range could not be separated clearly. None of the modifications in the air separation method, such as we were able to make with other methods, produced a decisive improvement in the separation of the finest whisker fractions.

A much more accurate classification was achieved with a dispersion method which utilized the magnetic properties of the whiskers.

The original whiskers from the whisker machine are put into an ultrasonic bath and are dispersed in inert liquids of varying viscosity. The liquid containing the dispersed whiskers is withdrawn from the surface of the bath by means of a hose pump where a magnetic separation device is installed in the hose leading to the pump which, for all practical purposes, quickly catches all dispersed whiskers. The liquid thus freed of whiskers is returned to the ultrasonic bath.

Depending on the intensity of the ultrasonic motion in the bath, or /16
resp. the viscosity of the dispersion liquids, the most diverse fractions of whiskers are obtained in this manner, especially very fine fractions in the micron diameter range and far below. The smallest moving particles have a diameter of about 0.3 micron.

Because of the restrictions ordered by the Ministry concerning research efforts with respect to imbedding polycrystalline whiskers into a matrix, whisker production was directed more toward the demands of program section 5; in this connection the production of iron whiskers in the whisker machine was carried out which promoted the formation of parallel bundles of whiskers which had grown together. This was necessary in order to obtain small rods with large internal surface for fuel vaporizers.

Later on, however, a better way having greater efficiency was found:

Whiskers having diameters that are not too large (1 - 20 micron diameter) are arranged magnetically in rows of equal length and in this condition are pushed together to form whisker bundles of varying thickness. By subsequent gentle provisional oxidation the whiskers fuse together in the rows and also with whiskers in the neighboring rows resulting in a relatively stable skeleton of oriented whiskers. By subsequent reduction of the oxide and sintering the whiskers fuse together metallically with the formation of a mechanically resistant skeleton which, for example, has a diameter of 1 - 10 mm and a height of 0.5 - 25 mm. This porous whisker material is produced from short whiskers which are no longer useful for other purposes; however, in this condition, it has many interesting industrial uses, such as catalysts for the combustion of smoke for imbedding into resins for the production of heat-resistant pressure-proof /17 materials for tools, for the vaporization of gasoline in the carburetor of automotive engines, for regenerator materials, and for collector and battery electrodes etc.

Program section 3

Preparation for mass production of improved or modified whisker types for matrix reinforcement

The effort of this program section was concerned with the development of new types of machines for mass production of polycrystalline metal whiskers.

The reason for this new development effort was the fact that it seemed more economical to develop a new, more efficient machine than to modify the original one for greater output of whiskers.

Our first whisker machine with an output of 1 - 1.5 kg of whiskers per day was probably the first whisker machine ever which provided the production of such relatively large amounts of whiskers. The development of this machine, which was preceded by a very long development phase, was also supported by the Federal Ministry and was intended to study whiskers as to their properties and to their application for the production of compact metals. For this earlier research the discontinuous production of whiskers in a reaction chamber was sufficient. Similarly the appearance of whiskers of varying dimensions was not particularly disturbing when used for the production of compact materials. It was also possible to show that polycrystalline iron whiskers could be /18 produced without disturbances and with low costs as long as the conditions for growth in the machine were properly controlled. Two machines of this type for the production of test quantities of polycrystalline iron whiskers have been in continuous operation for several years.

For the research tasks described in this report it became soon evident that whiskers made by the discontinuous machine had to be classified and that it was especially important to produce possibly long and thin whiskers. The appropriate separation techniques have been previously reported.

In order to apply the results of our research and development efforts for industry as soon as possible, it was necessary to prepare for production of whiskers in ton quantities and with uniform dimensions and properties. Although the discontinuously-operating original machine could be basically duplicated and although fine-dimension whiskers in the micron range could be produced by short-duration (several minutes) growth in the reaction chamber, the duplication of this machine for industrial production of whiskers would be too costly. Therefore we searched for ways to modify the production technique of whiskers and to make it continuous. For this purpose our previous extensive experience offered a number of good possibilities which we examined systematically as to their practicability.

A series of arrangements were created on a laboratory scale in order to study the individual processes. We came to the conclusion that, with a view toward future development, it would be most sensible to let whiskers grow on moving belts which receive the whiskers in a reaction chamber, then pass through a zone for quick metal deposition, and them transport them to a collection chamber where they are stripped from the carrier.

The following realizations can be gained for such a process: / 19

1) Polycrystalline metal whiskers can grow parallel to each other on a substrate.

2) The polycrystalline metal whiskers grown adjacent to each other on the substrate can be moved so close to each other that they form a dense satin-like covering of the carrier which thus constitutes a high concentration per unit area of whiskers.

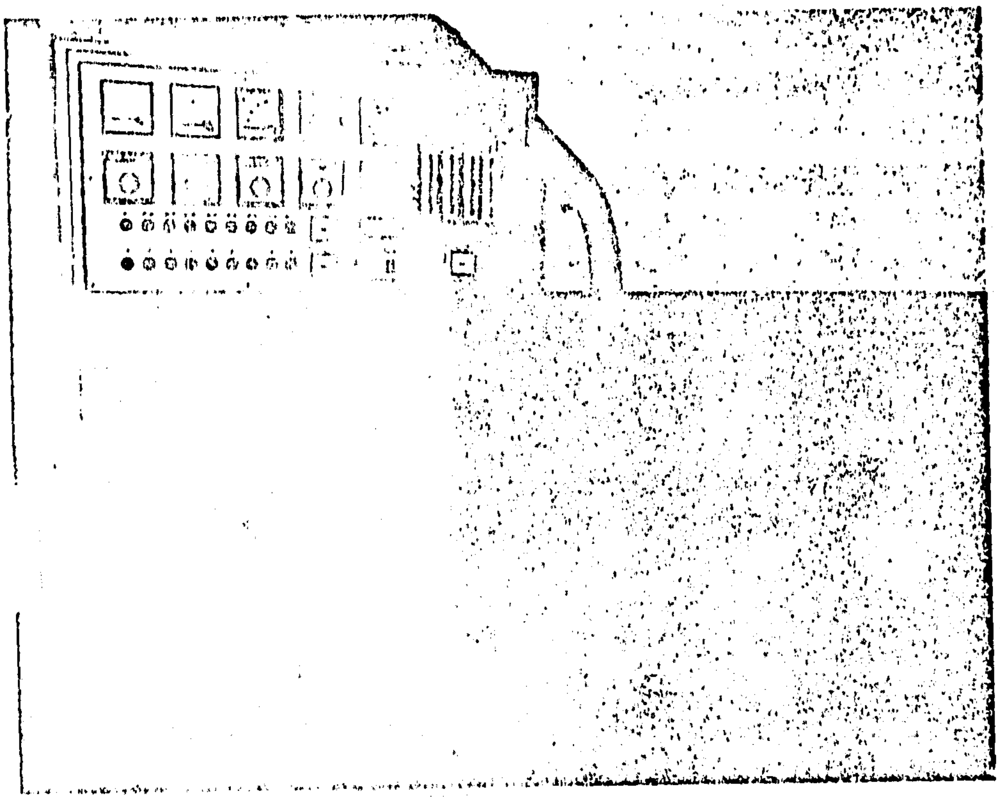
3) The very fine primary whiskers can be first maintained stable and parallel to each other by magnetic forces so that they do not tangle and they can then be heated on their surface to varying degrees for the purpose of continuous further separation of metal.

The primary, very fine whiskers with a diameter of about 0.01 to 0.1 micron are grown in a miniature filament formation process in a small seed chamber which then deposits the thus produced fine primary filaments on the moving band. The primary filaments can either be positioned upright on the carrier or lie loosely, fixed by magnetic forces. Their weight per unit area is 1/3000 to 1/10,000 of the weight of the ultimate whisker reinforced by metal deposition. One of the possibilities to utilize the heat of decomposition for the metallizing process (deposition of metal by thermal decomposition) is to heat the moving belt directly by resistance heating.

Our plan was to build the new whisker machine in such a way that, as a test device, it could produce 5 kg per day and that it could be extended for a production of 50 kg per day. This potential for increasing production comes about because an individual channel is provided for the production of 5 kg per day; this channel is several meters long, but only 15 cm wide. Ten such channels can be assembled in a production unit which has common electronic controls which regulate the temperature and other important parameters.

The following figure 3 shows the pilot machine for the production of /20
5 kg per day which, however, is only 3 m long instead of 7m because we did .
have enough room to assemble the complete machine. The control section with many units for monitoring was built to study the control possibilities of the machine and is thus somewhat oversized and will be simplified in a practical application.

Figure 3



By modifying the seed chamber used for producing primary filaments, /21
the magnetic field and the primary filament heating used for metallizing, it is possible to vary the types of whiskers that result. The present setup is aimed at producing, at first, only sufficiently large amounts of relatively short whiskers 1-2 mm long for industrial production of whisker heat exchangers in order to be able to utilize their valuable properties as soon as possible. The production of uniformly long whiskers about 5 - 10 mm in length and with a high L/D ratio should also be possible with this machine, as well as with other machines coming out of our development program.

Program section 4

Working methods for production of fiber-reinforced materials using polycrystalline whiskers

To produce a fiber-reinforced matrix one can introduce whiskers into a resin. With this method it is difficult to attain a high volume concentration of whiskers and the high-strength, but brittle whiskers will partially break up into smaller pieces. For very fluid resins it is more advantageous to impregnate felts or whisker networks which are bound to each other metallically.

Another method often used for other fibers to obtain felts is the filtration of fiber dispersions. For the filtration whiskers of possibly uniform dimensions were dispersed in a liquid such as methyl alcohol and, under constant stirring of the specifically heavy whiskers, were filtered through a filter plate
vibrating at a rate of 50 Hz. Of course, it is also possible to produce a /22
dispersion of very fine whiskers in a liquid of higher viscosity, such as paraffin oil, and to filter it without continuous stirring. The filter cake, after thorough washing, can be removed as a whole from the filter, dried, and then used for further processing.

Filtration alone does not produce a dense whisker material and thus, for matrix reinforcement, has too great a porous volume. To later compress the filter cake composed of originally hard and brittle whiskers is not advisable because of the danger that longer whiskers might break.

A more favorable method used by us for whisker depositions in the form of felts or mattes starting with oriented whiskers is centrifuging.

The whiskers are first hurled in a de-magnetized state against the centrifuge wall made of non-magnetic material where they are, just as in filtration, packed densely together. If centrifuging of the whiskers from the dispersions takes place in a homogeneous magnetic field parallel to the axis of the centrifuge, then the magnetic whiskers will be oriented parallel to each other, in the same direction as the magnetic field. On the other hand, a magnetic field which is tangential to the circumference of the centrifuge, will produce orientation of the whiskers parallel to the circumference.

After removal of the dispersion liquids the whiskers, still in the centrifuge, can be cemented to each other by metal deposition, preferably by deposition of the metal from the gas phase. Here nickel is to be preferred.

The thus resulting whisker skeletons can also, still in the centrifuge, be impregnated with a resin and depending on requirements can be hardened more or less completely.

After the centrifuge has come to rest the centrifuge container can /23
be disassembled so that one can cut away and stretch out the whisker-filled resin covering the wall.

In this way, with numerous procedure variations, whisker-reinforced plates of various resin matrices or only plates of whisker skeletons can be produced simply for subsequent impregnation.

Industrial firms were primarily interested in the questions whether extrusion of whisker-containing thermoplastics is possible and whether the extrusion apparatus would be appreciably damaged thereby. To be very direct: the latter has not yet been determined.

Preliminary experiments for impregnating whiskers in thermoplastics through hot-pressing or resp. for extrusion were first conducted by us. Here we employed a method used by us in the production of compact materials from whiskers for making experimental rods where we filled thin brass or steel tubes with a mixture of whiskers and thermoplastic granulated material, closed off the ends, and after sufficient heating under high pressure, quickly flattened them out. After removal of the deformed tubes, flat bars of whisker-reinforced thermoplastic were obtained.

These experiments achieved that, for higher pressures, the thermoplastic transfused completely through the whiskers and penetrated even into the smallest spaces of the whisker network in the range of several microns.

The actual industrial extrusions were conducted expertly by the firm of Gebrueder Buehler, Uzwil/Switzerland, since they had available small extrusion presses and they were able to give us all kinds of help including testing of the material.

These tests which had to be conducted at the convenience of the Buehler Co, /24 produced some encouraging results although they have not yet been concluded. They are being continued with improved whiskers and with continuing study of the bonding of whiskers to the thermoplastic matrices. Even the method used for introducing the mixture of thermoplastic granular material and whiskers can be improved. The extrusion tests were more time-consuming than expected because the tests set up in advance for the investigation of the most discriminating influence parameters were too few in number. In order to further pursue the very promising path of extrusion one must attempt to make the research program more extensive.

As an example, the usual methods for attaching thermoplastics to metals are not necessarily good for whiskers. Attempts to bond whiskers to Polyamid 12 using the industrially proven adhesives for iron or steel, conducted by the firm of Emser-Werke (producer) themselves, gave no convincing results.

On the other hand it was possible to attain the following property improvements with a new and valuable thermoplastic "Ryton" (polyphenylene sulfide) which could also accommodate well fillers of iron oxide:

Increase in bending strength	85%
increase in tensile strength	215%
increase of E modulus	318%

The whisker content was 20 volume percent just as in all other tests.

While there was a tendency to judge the worth of a whisker-filled composite primarily by the increase in tensile strength, surprisingly there was considerable interest in the increase in compressive strength of heat-resistant resins by the use of whiskers. The reason is that, for some time now, industry has felt the need for inexpensive tools which are suitable to stamp out plastics or sheet metal in not too large production quantities. Such an example is a press for a chassis which cannot necessarily be produced in mass production so that the presses for tooling become an enormous investment. In contrast, the relatively inexpensive bonding material made of whisker-reinforced resin provides considerable savings. /25

Such tools are basically not new, but the remarkable advantage of metal whisker reinforcement lies, among others, in the sufficiently high mechanical strengthening, along with extensive heat removal by the heat conducting whiskers which, for heat removal, can be installed magnetically in an advantageous direction.

The resins used were heat-resistant epoxy resins or lately polyimid resins. Polyimid resins having very favorable work properties have been developed for the just described application and far beyond by Technochemie Heidelberg. These resins are very fluid and allow a high degree of filling the whisker composites, especially in those cases when the often-mentioned whisker skeletons are to be used for impregnation. Such bonding bodies made of polyimid resins and polycrystalline metal whiskers have a long-time heat resistance of at least 250°C.

In addition to all other interesting applications of fiber-reinforced matrices which, in the future, can result from the preliminary efforts, the use of whiskers for the production of pressure-proof composites for punch press applications could presumably require a great amount of whiskers. As described, the whiskers are an aid in reducing the high required investments; this /26
emphasizes the need to strive for a cheaper mass production of whiskers such as has already been considered for whisker heat exchanger applications.

To a limited degree we also conducted tests to impregnate iron whisker skeletons with pure magnesium since this seemed to be one of the possibilities to strengthen magnesium effectively and, above all, to increase its thermal stability.

Impregnation of whisker skeletons was not possible with untreated oxidized whisker surfaces, but for a freshly reduced whisker surface the magnesium, under vacuum, penetrated the whisker network and filled even the smallest interspaces in the micron range excellently.

Although there was great interest, this process could not be carried on as large a scale as hoped by a light-metal company because of the supposed danger of the impregnation procedure. Therefore, test bars could not yet be produced; however, we expect to continue the work on the present basis and, when the time is ripe, to put in operation an impregnating installation at the Buehler company.

Program section 5

Procedure for production of special materials from whiskers as a solution of real scientific-technical problems

As far as we can see today, one of the most pressing important applications of polycrystalline metal whiskers is their use in the form of skeletons or networks. Such whisker skeletons are produced very simply by pouring the rod-shaped material loosely unto a surface or, after pouring out subsequently compressing them and finally joining the whiskers to each other at the points where they touch.

In rare cases this will take the form of cementing with resins or /27
the like; in most cases, however, it will be a case of the whiskers growing together metallically. For this purpose the whiskers are sintered to each other or are combined with each other by metallic deposition at the points of contact.

Because of their low cost we primarily used unalloyed iron whiskers for our tests and developments.

The sinter process produces a whisker skeleton where the unalloyed individual whiskers suffer, more or less, from a reduction in strength and hardness, but experience an increase in ductility.

Because the cores of iron whiskers are extremely small (80 to 90 Å), there is a lot of room for core growth as long as this is not suppressed by well-known measures (e.g., foreign substance dispersion). Whiskers in the micron size range can be readily sintered at temperatures as low as 600°C. For producing sintered skeletons from whiskers all methods and aids from powder metallurgy can be used with advantage such as moistening the whiskers before compression to improve their ability to slide.

Impregnation of the whisker skeletons to be sintered with liquids, such as alcohols, aids in bringing the whiskers closer to each other because of the effect of capillary forces. The same effect is achieved by premagnetization of iron whiskers which, because of magnetic attraction, produces close networks.

Sintering of networks from whiskers generally occurs between 800 - 1100°C for iron whiskers and 700 - 900° C for nickel whiskers.

A fast sintering of whisker skeletons can be carried out in a high-frequency induction field (we used 1 M Hz) since this heats such a network not only externally, but the heat penetrates deeply. Sintering is done in a vacuum or in a N_2 or H_2 atmosphere, for certain applications also with air supply whereby the whiskers are joined to each other with a thick oxide layer.

The combining of polycrystalline whiskers to a network, starting with /28
a loosely or a more or less densely poured material, is carried with great advantage by chemical metallic precipitation from the gas phase. The most striking advantage of this method can be found, above all, in the fact that polycrystalline iron whiskers whose strength is not reduced until temperatures of 300 to 400° C are reached, can be joined to each other mechanically far below

this temperature by metallic precipitation without loss in strength. The metallic precipitation results in a certain thickening of the whiskers where, at the points of contact, whiskers are joined to each other in a way which can otherwise only be done by prolonged volume sintering. This skeleton formation through metallizing thus represents a direct transition of loose whiskers into a network without adversely affecting the original strength of the polycrystalline metal whiskers.

For the production of networks through metallic cementation the same type of metallic combination is generally used as that which produced the original whisker, namely a metal carbonyl. To decompose this metal carbonyl at temperatures between 140 and 250°C the whiskers must be heated discontinuously or continuously while the vapor of the metal compound flows through the network. The whisker network is heated by flooding it with an inert hot gas, for thin layers by conduction; it can also be done by induction heating or resp. by direct resistance heating. Induction heating and resistance heating have the advantage that the heat of decomposition of the metal compound can be readily proportioned.

Application of whisker networks /29

Before discussing the technical applications of whisker skeletons which we have developed let us summarize and characterize the structure and the properties of whisker skeletons.

In contrast to sintered powder metal with its relatively small pore volume the sintering of small rods, i.e. whiskers, produces a highly-porous structure which, without any difficulty, can comprise 95% or more of the whisker network. Such a highly porous volume in a metallic network can be utilized to advantage only because the building blocks of the network, namely the whiskers, consist of a far-above-average strong material. Networks consisting of fine, cut metal wires are theoretically feasible, but because of the high cost of wires in the micron size range are not practical. The polycrystalline metal whiskers, on the other hand, are considerably cheaper.

It is especially useful if a whisker network has a very high internal surface so that the flow of a gas or a liquid can readily take place without appreciable flow resistance.

The following figure 4 shows the relation between total whisker surface of a network and whisker diameter. /30

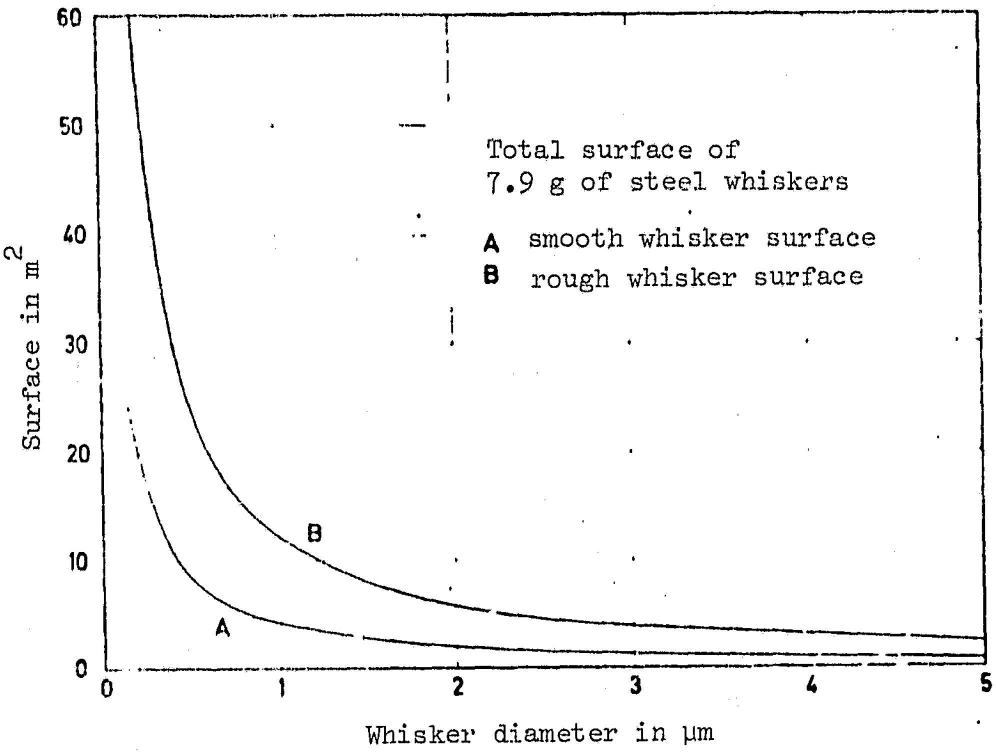


Figure 4

Using whiskers with diameters of a few microns or less we obtain available surfaces of many square meters for 1 cc of iron, or 7.85 g of iron resp, which can be imbedded into a whisker network. Obviously, in comparison, powder metal of such fineness theoretically produces a still greater surface, but this cannot be practically utilized either with a loose or with a sintered metal powder to the same degree as with a wide-mesh network of filaments. The achievement of a large inner surface of a whisker network is also aided by the fact that the polycrystalline metal whiskers are generally not smooth, but have a very grainy, rough surface and that this surface roughness can be increased considerably during the whisker production process or later.

Additionally the very good electric conductivity of a whisker skeleton must be emphasized which makes it possible to conduct relatively high currents. /31

Such whisker networks should be especially ideal for electrodes for batteries and fuel cells. The battery, especially the nickel-iron or nickel-cadmium battery requires a self-supporting strong and highly porous metallic skeleton in which the active material is put in such that it is in good contact with the electrolyte as well as with the conducting supporting structure of the electrode. The great innate strength of the polycrystalline metal whiskers, the fine branching of its network into the poorly conducting active material and the cementing of the network through mechanically strong and well-conducting metal deposits promise the formation of an effective electrode with a saving of weight and volume.

Thus we examined the possibility of producing polycrystalline metal whiskers with regard to industrial production.

Porous mattes of whiskers can be prepared in the usual way by filtration of suspended metal whiskers. A more effective method is the precipitation from a suspension in a centrifuge since, in this way, a dense and uniform packing of the whiskers can be achieved. Also the deposition of the whiskers on the centrifuge walls can be oriented in a preferred direction by means of magnetic fields, such as parallel or normal to the centrifuge axis.

The metallic cementing of the polycrystalline metal whiskers can even be carried out inside the centrifuge as well as the introduction of the active material into the skeleton.

In a similar way the electrode skeleton for a fuel cell can be prepared. /32
The electrode for a fuel cell generally requires pores of a definite size which are to be found in a possibly strong, but well-conducting metallic supporting structure. Here the uniformity of these pores is of considerable importance; this can be achieved with fine whiskers in the micron range. For the surface treatment of the whisker by galvanic metal precipitation a centrifuge was also employed. Here the wall of the centrifuge served as the cathode against which the whiskers were hurled periodically from their dispersion in the electrolyte.

Here newly deposited whiskers become the upper cathode layer, immediately available to the ions. By this method of precipitating metals on whiskers electrochemically it is possible to cover nickel or iron whiskers, for example, with porous nickel, with silver, or with other suitable metals.

The thought occurs to sensitize the whiskers which form the mechanically strong network of the cathode by precipitation of layers of high porosity and of known catalytic effectiveness, such as a precipitation of nickel boride or a coat of Raney metal formed from whisker material. The carrying out of this treatment of polycrystalline metal whiskers so important for fuel cells had to be postponed because of the urgency of other projects described later.

Furthermore the investigation of the suitability of polycrystalline metal whiskers for exhaust gas catalysts was considered to be as significant as the work with skeletons for battery and fuel cell electrodes.

As is well known, the first 200 seconds after the start of an automotive engine are the most critical for judging the pollutant content of the exhaust gases.

Because of its thermal inertia, the catalytic afterburner requires a /33
definite amount of time to reach its operating temperature. The support structure for the catalytic afterburner is generally a loose ceramic assembly with a highly porous, catalytic surface or, resp., a structure made up of parallel capillaries with a honeycomb-shaped cross section. One might at first not expect that a whisker network of polycrystalline metal whiskers as catalyst support would have sufficient volume to pass the considerable amount of exhaust gases generated by the operation of an automotive vehicle. However, the polycrystalline metal whiskers make this possible if they are joined together in a preferential direction; this can be accomplished by joining them together in a magnetic field. Such whisker systems possess a surface structure which provides for better gas flow and a more rapid diffusion than ceramic honeycomb catalysts. The entire available surface of the whiskers can be coated with a thin layer of a catalytically effective material. To date we have only deposited platinum. Iron whiskers as catalyst carriers can be converted into a thermally stable oxide which can withstand temperatures of 1000°C. Further efforts

will be concerned with covering the oxidized whisker network with metallic or ceramic coats. As far as can be determined today the catalytic afterburner made of whiskers has the following advantages:

1) The catalytically active surface directly available for a rapid gas flow is greater than that of ceramic catalytic converters.

2) Because of the small mass of the freely available whisker material the time required to increase the temperature to its fully effective catalytic temperature is shortened considerably.

3) The whisker catalytic converter should be considerably cheaper than the conventional ceramic honeycomb converter. /34

The present disadvantage of the whisker catalytic converter is found in its yet insufficient mechanical strength which is the result of the brittleness of the oxidized metallic whiskers as they are joined to each other.

The whisker catalytic converter for automotive exhaust gases can only be further developed in cooperation with an automotive manufacturer since, in addition to measuring its primary catalytic efficiency one must determine its behavior under practical operating conditions. As an example this will include the ability to hold up under vibrations, the behavior during intermittent thermal loading caused by peak temperatures, its ability to respond to changing conditions and many others which can furnish valuable information to the engineer.

In the meantime we were approached by industry to address a similar problem of environmental protection, namely the ultimate combustion of flue gases. Here the problem of testing the effectiveness of the whisker catalyst is less involved than in the case of the ceramic honeycomb catalyst which is also used for combustion of flue gases. Although the operating conditions of the catalyst for flue gas combustion are not necessarily the same as those of the automotive converter, the activity of the catalysts made up of whiskers is comparable.

The burning up of flue gases requires a catalytic converter of large diameter and short height because flue gas flows of 500 - 1000 Nm^3 per hour must be processed in small devices with a pressure drop of no more than 30 mm of water. The operating temperatures of the catalyzer activated with noble metals lie between 350 and 450°C.

The models of flue gas catalytic converters which we fabricated in /35 several versions proved to be as effective as honeycomb catalyzers of conventional construction.

As an example, for a working temperature of 450°C we measured 0.05% CO in the exhaust gas. The catalytic material on the whisker skeleton which constituted the carrier structure, was a thin coat of platinum which was generated by thermal decomposition of a platinum compound solution wetting the skeleton.

Additionally we found that at 600 - 700°C a whisker network is effective even without platinum deposits since an effective combustion reaction is maintained within the pores of the whisker network. In this case the network was heated externally by a flame.

Heated by a gas flame the whisker catalyzer was able to burn, with a blue flame, dense smoke generated by a low-temperature saw dust burner. As will be reported later, an economically burning, non-smoking blue heating flame can also be generated from light heating oil with the aid of a whisker heat exchanger; this flame can be used to heat the whisker skeleton designed for the combustion of flue gases.

The advantage of developing a whisker catalyzer for combustion of flue gases is to be found in its much lower fabrication and exchange costs compared to the ceramic honeycomb catalyzers.

There is no doubt that in the future a great portion of the flue gases generated by industry must be cleaned up as well as possible before letting them escape into the atmosphere. According to our information there is a very considerable number of factories in Germany which are interested in flue gas cleanup. Alone 30,000 smoke houses are included in this number.

Undoubtedly the necessary high investments for flue gas combustors can be reduced appreciably by less expensive catalyzers. In a certain sense this situation can be compared to that of the automotive exhaust gas catalytic convertor. /36

In addition the salvage of platinum as active catalytic material for low-temperature combustion from a poisoned catalyzer is a much simpler operation than from a ceramic carrier material.

The most valuable contribution which we can make with the use of whisker skeletons concerns the whisker heat exchanger for the preparation of diesel oil, light heating oil and gasoline.

We first studied in simple devices to what extent fuels can be heated and vaporized in whisker skeletons in a matter of a few seconds. Likewise we attempted basically, with preheated whisker skeletons, to vaporize heating oil or, resp., to change it into a very fine mist; we then mixed this mist turbulently with compressed air and by combustion of the resulting good mixture we, for the first time, obtained a blue flame. We carried over this test result to an oil burner and in a short time with suitable mixing of oil mist and air we were able to generate more or less good blue flames.

Both results, that of creating a very fine gasoline mist and of producing blue flames seemed to be of remarkable interest with regard to the serious problems of fuel preparation for automotive engines and with regard to combustion of heating oil in conventional oil burners. Everybody knows to what extent people had to resort until now to utilize the various measures that were available to produce a better combustible mixture in both cases. All these measures, in the end, are not satisfactory to date, but they had to be investigated because they were promising and did not lend themselves to advance calculation.

The more information we obtained from experts in sectors of the automobile /37
and oil burner industry concerning the conventionally used measures and processes for mixture preparation and combustion, the more complicated the interaction of many parameters seemed to be and the more understandable the present difficulties seemed to us. Above all, the most difficult feat in automotive

engines seemed to be the uniform introduction of the mixture of air and fuel droplets from the carburetor venturi into the cylinders; for the oil burners the intensive mixing of the atomized heating oil droplets with combustion air and the timely complete combustion of these droplets seemed to be most difficult.

With regard to this problem the use of whisker heat exchangers for producing finely divided fuel particles was not only a new procedure, but also a preparation for the ultimate solution inasmuch as fuels could finally be broken by the whisker heat exchanger into such fine droplets - and in a technically simple manner - that condensation of such droplets on the wall was greatly or even completely eliminated.

In the opinion of all leading oil burner manufacturers, boiler manufacturers including some firms from the steel industry which are interested in heating their blast furnaces with oil, the whisker heat exchanger promises, as one of few potential possibilities, to make possible, in the near future, the realization of the improvement in oil heaters required by law.

Although this working principle for the preparation of fuel mixtures using whisker heat exchangers seemed simple at first, our efforts to reach a technically sound solution from the recognizedly good working principle, finally were very time-consuming and costly. The following reasons were /38
responsible for this: the heating of a flowing liquid in a skeleton made up of very fine filaments had only been investigated to a very limited extent to date; problems of heat transfer, electrical contacts of such a skeleton, and the separation of products of reaction in the pores of the whisker skeleton; determining the proper electrical resistance, and finally questions as to the economics of the procedure. A final important problem was the accommodation of the operating conditions to the installations already in use for conventional oil burners and the monitoring of these functions.

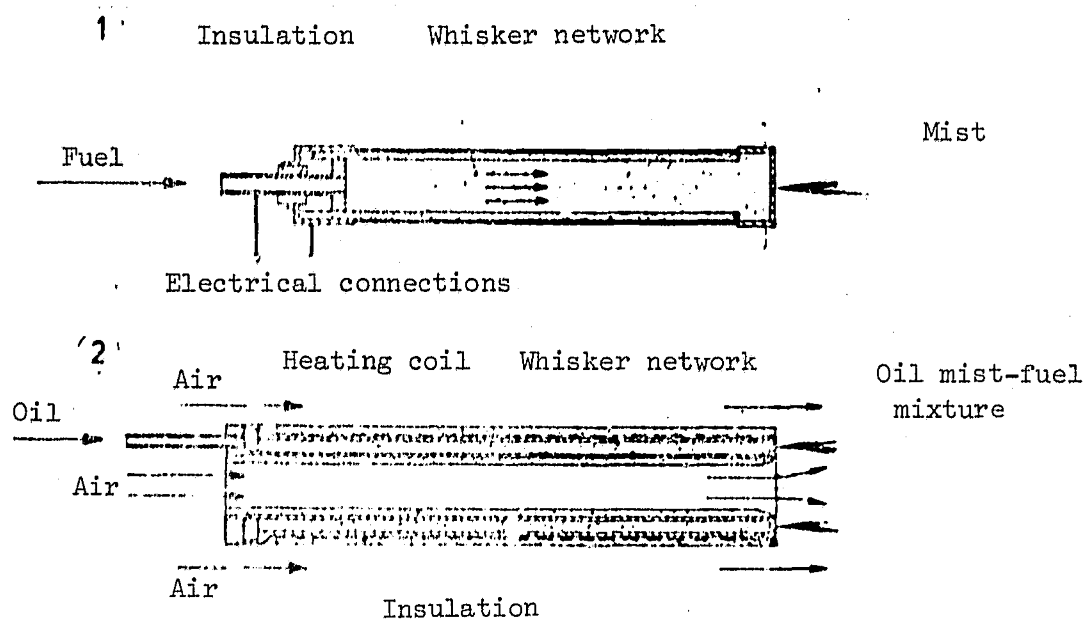


Figure 5 - Directly and indirectly heated heat-exchanger (principle)

The above figure 5 shows the principle of the whisker heat exchanger. /39
With the aid of the figure we shall describe how the preparation of heating oil takes place in the simplest case:

The whisker column is placed in a steel tube and insulated from it except at the bottom where it touches it and thus makes electrical contact on this end. The other end of the whisker column, still inside of the insulating hull, is contacted by a perforated metallic electrode. An electrical current, on one side connected to the perforated electrode and on the other end to the bottom plate of the enclosing steel tube, heats the entire whisker column, through direct resistance heating along with its hundreds of thousands fine branches; this extremely-finely branched whisker network then gives up its heat directly and very fast to the penetrating oil.

In this whisker column are found different aggregate-states since the liquid is changed continuously into mist and into vapor. Since heating oil is a liquid which is composed of hundreds of different carbohydrates, a multiplicity of boiling points arise. Thus the heating oil while flowing through the whisker heat exchanger does not pass, in a given zone, spontaneously from a liquid to a gaseous state, but a great number of different boiling points are reached in the column. The initial boiling takes place at about 60°C while the first appreciable vapor formation occurs between 160-170°C. The following figure presents the various boiling fractions of Diesel oil, somewhat comparable to light heating oil for which we have no values.

/40

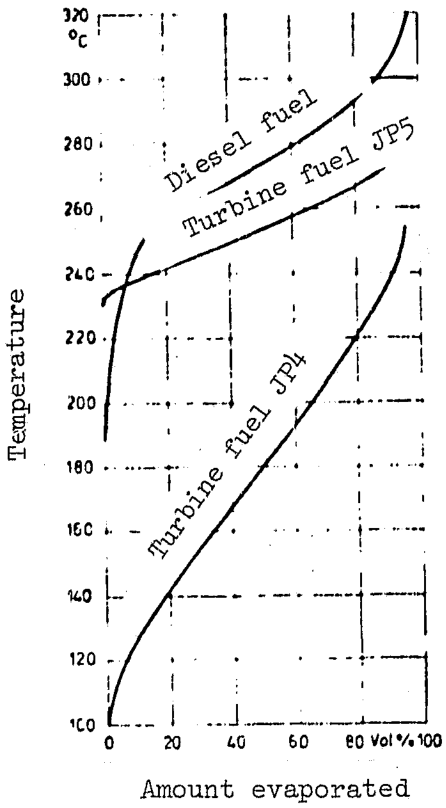


Figure 6 - Boiling curves of Diesel and turbine fuels

Although near the end of the heated whisker column the greatest part of the heating oil is converted to vapor if sufficient heat has been added, one must make sure to vaporize even the highest boiling last fractions of the oil since, above 350°C, cracking can take place. These last high-boiling fractions of the heating oil thus must be blown out of the whisker skeleton in the form of very fine droplets with the aid of the already appreciable vapor pressure.

Before discussing the development of the heat exchanger itself, which has led to several practical potential applications, we must emphasize that understandably the conventional oil burner was not prepared for an improved system of producing very fine mists of this type. Until now extremely fine mists could only be achieved through atomization under very high oil pressures which, for the atomizing orifices then in use remained constant for a given flow rate. These pressures, as an order of magnitude, lie between 11 - 16 bar. On the other hand, to operate the whisker heat exchangers, relatively low oil pressures were needed, i.e. initial pressures of only 0.5 bar or lower. This initial pressure, however, increases at the present state of the art continuously after several hundred hours; after 1000 hours of operation the values reach about 8 - 9 bar. This pressure increase results from the contamination, as yet unavoidable, of the whiskers by products separated from the oil whereby the pores between the whiskers are gradually decreased although this occurs only in a preferred zone near the hot end. /41

This would be no problem if a hard pump could be used to push the oil through the whisker heat exchanger, such as possibly a piston pump which, regardless of pressure drops, could maintain the preset quantity of oil. Although this presents no problem for the pump manufacturer, the mass production of gear pumps has reduced their cost so much that, at present, a cheap substitute for the gear pump cannot be realized. /41

Although the choice of the pump originally was not our problem, it soon became ours because we received no help in this matter and could not afford to let the development of the heat exchanger fail because of pump problems. This led to a compromise whereby a conventional oil pump delivers the proper amount of oil, as before, through a conventional atomizing nozzle which, however, was installed simply, as a flow-control capillary, in the tubing between the oil pump and the heat exchanger. This is undoubtedly a temporary solution, not a permanent requirement.

The example of the oil pump shows that we were not able to develop the whisker heat exchanger to its completion with a free choice, but that we necessarily had to be content with what was available in conventional oil burners, namely the pump, the low-pressure lift, the disturbing high-volume /42 ignition electrodes and the flame-out detectors which required a yellow flame. Today we know that it is not complicated to construct an ideal oil burner of a new design which, in all its auxiliary functions, is designed for use in whisker heat exchangers. But in order to demonstrate and implement the new principle of oil burners, and also because of the possible need to convert conventional oil burners inexpensively to our economical system, it was advisable to make this temporary compromise. This became a necessity when we discovered that the entire oil burner industry which we consulted did not consider themselves to be in a position to take over the development of an oil burner following our new design by themselves since this branch of the industry is primarily concerned with installation rather than development efforts.

However, we believe that we can demonstrate in this report that, in the end, it was worthwhile to take on all necessary development efforts for the oil burner since we now have complete operational test samples of blue-flame burners which show the superiority of our system over all other no less expensive test systems which now can be copied by the industry and be sensibly improved; this may already be under way.

Research and development of whisker heat exchanger /43

It was evident from the beginning that, from a physical standpoint, the direct resistance heating of the whisker column was the most rational approach. This assumes, however, that it is possible to produce a skeleton of whiskers with homogeneous porosity and conductivity, that it is possible to make good electrical contact with the whisker skeleton and that certain material problems could be solved.

The whisker skeleton was shaken into a tube made of E-glass, quartz, or ceramics and, if necessary, was sintered. The contact was improved appreciably by subsequent metal deposition, from the gas phase, on the hot end, i.e., where the fuel vapor exits; in this way the whiskers were practically cemented to the contacting wall. This good contact did not fail even for very high currents.

On the cold side of the whisker column we first used an adjustable contact in the shape of a drilled-through steel bolt; however, later on we found a more satisfactory contact which consisted of a perforated nickel-coated brass block which contacted the whisker under spring tension. In order not to endanger this contact spring by high currents, it was bridged by a copper cable.

Since in such a whisker column faulty contacts cannot always be avoided which then, because of current constrictions, lead to overheating, the contacts between the whiskers themselves were improved by subsequent metal coating.

The quality of the whisker skeleton as a conductor of heat depends, among others, on the proper sizing of the whiskers and, of course, also considerably on the manner in which the whisker column itself is produced.

We found that it is much simpler to produce a good whisker column /44
for a whisker heat exchanger by producing shorter pieces and them joining them together. It is anyway necessary to keep them under a definite spring tension in order to assure good contact at the cold end.

Since we were always looking toward later industrial production, we also produced heat exchangers whose whiskers were not sintered, but touched each other under pressure. In general the electrical contact was quite good, but later the contacts were contaminated by deposits from the oil. In these cases local overheating occurred. For this reason the direct heating of the whisker column was modified by installing very thin V2A tubes into the whisker column so that the heating current passed simultaneously through the steel tubes and the whisker columns. These whisker heat exchangers, heated by resistance heating, underwent constant improvement efforts in order to assure reliable operation. This type also retains its worth for the preparation of oil in greater quantities.

For the useful application of whiskers in heat exchangers for the combustion of heating oil in smaller quantities, such as residential heating, a serious obstacle to its practical utilization appeared. The whisker column, because of its great conductivity, naturally has such a low internal resistance that a high-current transformer is needed for its operation. This costs many times what a heat exchanger costs and thus, from an economics standpoint, must be considered a serious handicap to a practical application.

For this reason we first attempted to increase the resistance of the whiskers which, however, seemed possible only by coating them since we found no way to alloy them in order to produce an extremely high specific resistance. In this connection we had previously observed that the oxide coating of oxidized iron whiskers is unusually dense and strong. This must be caused by the very /45 fine grain size of the whisker material. Therefore we worked out methods to achieve a controlled oxidation of the whiskers. Sometimes we completely oxidized the whiskers and then, by controlled reduction, achieved the desired low conductivity. Both were effective in principle, but the semi-conductor (poorly conducting) properties which occurred were so disturbing that, at first, we could not see when our goal of a greater, reproducible resistance could be realized. Thus we attempted a compromise in order to achieve a definite resistance for the heat exchanger column. The compromise consisted of building up the heat exchanger column alternately with 2-3 mm thick plates of whiskers and with tablets of porous bodies with a high specific resistance. In this case the actual heating was effected by the tablets of high resistance which were contacted to each other electrically by the higher-conductance whisker tablets. The whisker tablets, positioned the heating tablets of high specific resistance, were heated indirectly by conduction and then, across their large surface, transferred the heat to the oil flowing through them. This system worked very well with graphite tablets as far as heating effectiveness and resistance control were concerned, but we were unable to find a suitable material for the heating plates having very high resistance of the order to $x \cdot 10^5$ ohms. For that reason we developed our own material which could be produced with cardboard-like strength and from which the tablets with the necessary specific resistance could be stamped out. This material was also heat-resistant and consisted of a graphite network which was supported mechanically by a matrix.

However, during constant operation of the heat exchanger built up from /46 tablets occasional local overheating occurred, apparently caused by overloading of the contact surfaces between resistance and whisker tablets. Since this overloading occurred only after long-time continuous operation with heating oil, we concluded that it was caused by a gradual contamination. However, occasional disturbances of this type cannot be tolerated in the operation of an oil burner heat exchanger. Therefore we improved the whisker contacts by various techniques and whenever new models of heat exchangers were tested in oil burners we checked the effectiveness of these expedients. The following techniques were investigated in order to achieve uniform aging of the contacts between the fine whiskers and the low-conductance bodies:

1) Before being processed into tablets the whiskers were cleaned ultrasonically and with water solutions, and were then nickel-plated from the gas phase.

2) The whisker tablets were produced by quick-sintering, then were metal-plated on the front face with nickel from the gas phase, by galvanic deposition or by current-free precipitation.

3) The high-resistance tablets were nickel-plated from the gas phase on their front faces.

4) The front faces of the whisker tablets were covered with a disc of metallized glass-fiber gauze or with a metallized carbon gauze to serve as contact promoters.

5) The whisker and high-resistance tablets were cemented together with a heat-resistant conducting lacquer.

6) Perforated nickel foils of about 15 micron thickness were inserted between the whisker and the high-resistance tablets.

Of course, in all these various contact techniques care was taken that /47 the perforated resistance tablets and the contact improvers did not impede the passage of the oil.

With this system it was actually possible to produce heat exchanger columns with suitable resistances so that an intermediate transformer was not needed and the heat exchanger could be heated directly by a "Triac" (Variac?). Thus we achieved our goal to add the heat exchanger to all the other devices necessary for successful operation of the oil burner.

The following figures 7 and 8 again show an older-model whisker heat exchanger with direct resistance heating of the whisker column, identified by the large-size connectors for high current flows and then, in contrast, the relatively slender whisker heat exchanger with a column made up of tablets.

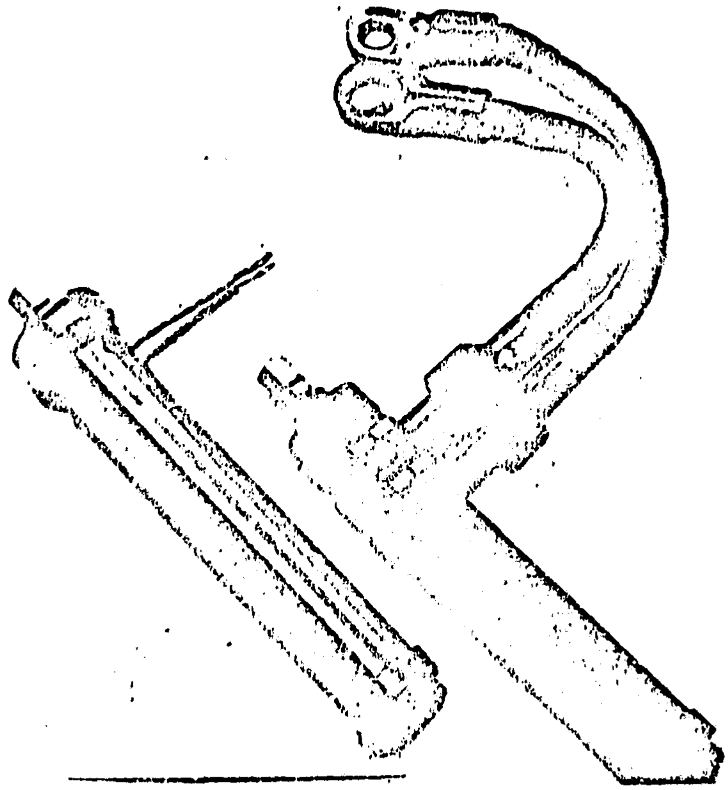


Figure 7

/48

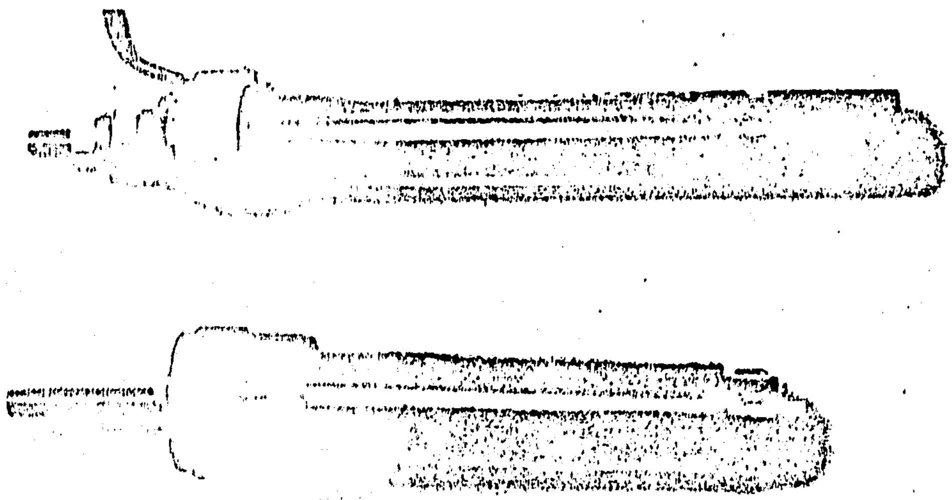
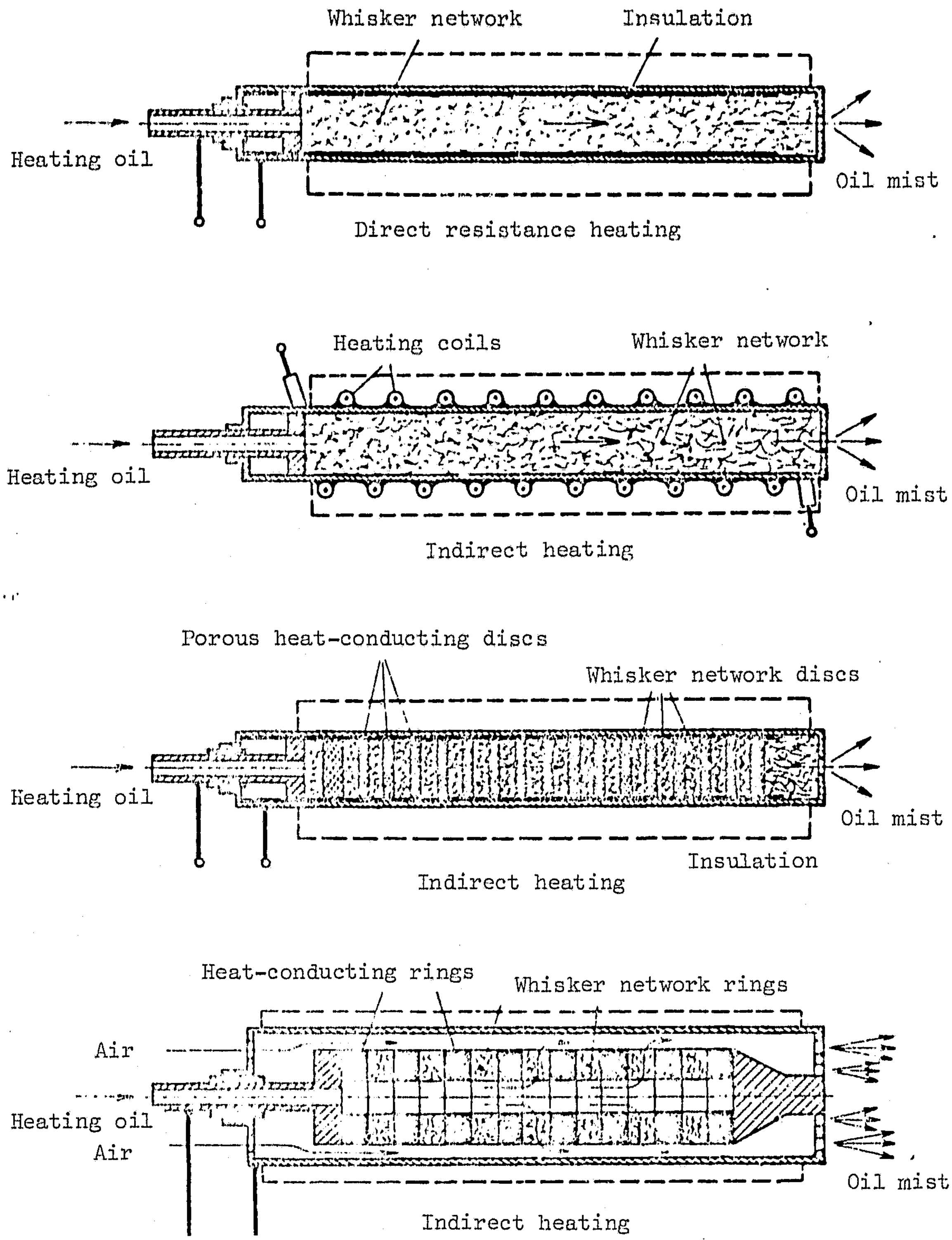


Figure 8

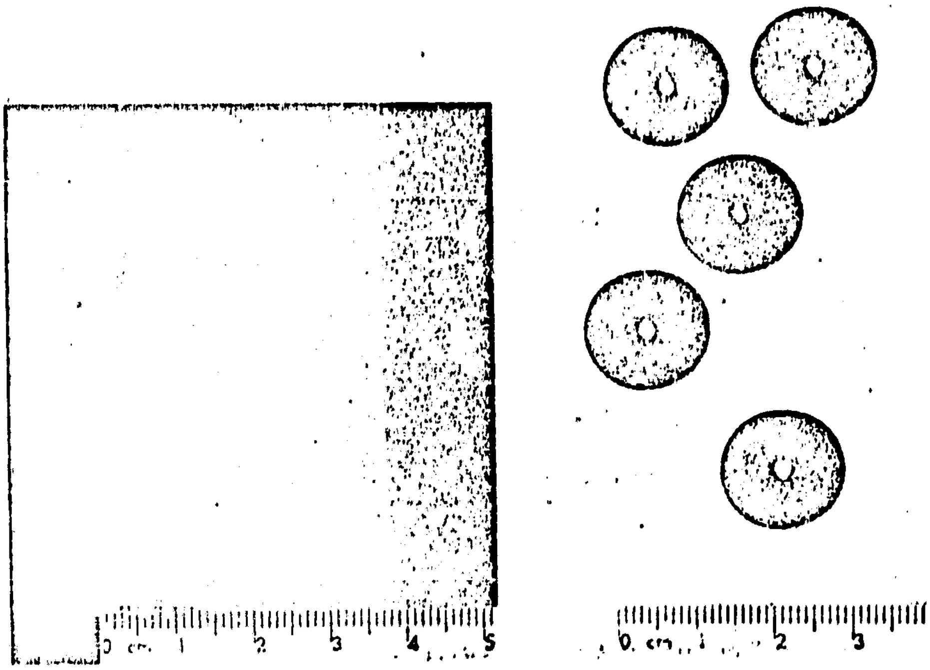
All these versions, of course, still are in need of an insulating shell which is required to avoid unnecessary energy losses since the oil burner heat exchanger is surrounded by cold combustion air.

In addition, a special type of heat exchanger made up of whisker tablets and heating tablets was produced in order to slow down the gradual closing of the whisker pores by deposits from the oil. In this construction the oil does not penetrate the entire tablet stack but leaves the whisker column by the shortest path by means of drilled-through passages in the tablet stack normal to the individual tablets. This heat exchanger which we first called cross-flow nozzle not only has very low resistance to flow, but also avoids the need for the oil to flow through the heating tablets. Above all it has the advantage that the oil can flow radially through the whisker tablets through an ever increasing pore volume. The principle of such a cross-flow nozzle is shown as the last example in the listing of various heat exchanger types shown in the following figure 9.

Fig. 9 Types of whisker heat exchangers with direct and indirect electrical heating of whiskers.



The following two figures 10 and 11 show examples of whisker and heat-conducting tablets that were used. /50



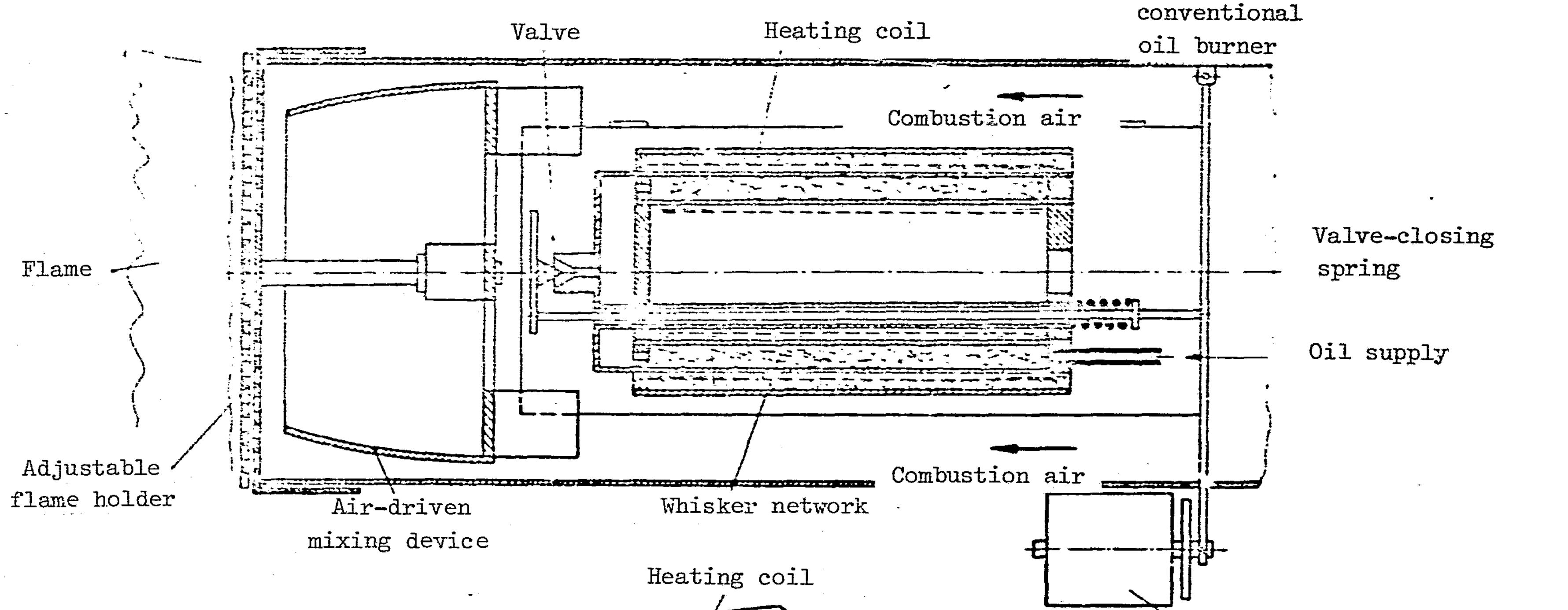
Figures 10 and 11

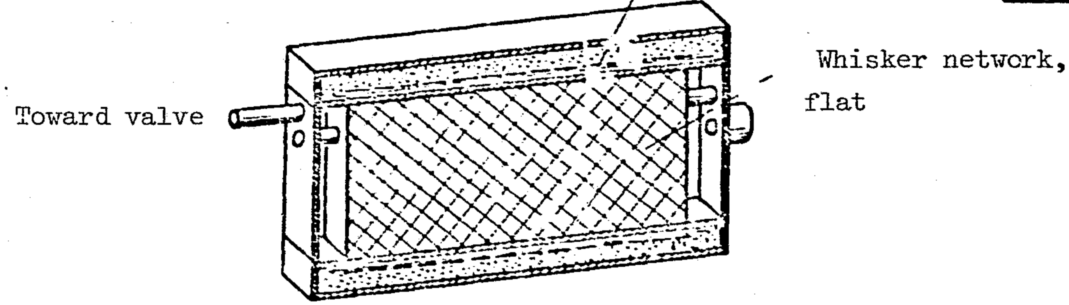
All these developments of heat exchangers, constructed and tested in an effort to achieve a reliable system for un-monitored oil burner operation, performed satisfactorily in the laboratory under constant control. However, since, warned by oil burner manufacturers, we provided for rough testing by outside sources outside of our laboratory, defects showed up where, during control of the heat output of whisker heat exchangers occasional overloads and damages of the contacts occurred. Thus, to a certain extent, the whisker contacts could not cope with a specific current strength. Until reliable automatic controls could be developed, overloads occurring in outside tests using manual control could not be avoided and could also not be controlled /51 by us belatedly. Thus, to play safe, we developed an additional type of whisker heat exchanger, namely one with indirect heating of the whiskers.

The principle of the indirectly heated whisker heat exchanger is shown in the following figure 12 in two versions. The first version shows a sectional view of the flame tube of a heating-oil burner. This type of whisker heat exchanger consists essentially of a circular whisker column (4) which is located, in close contact, between two tubes (5) and (6). The circular whisker column is heated by a heating coil (8) and is supplied with oil through the tube connection (12). The oil vapor or oil fog, resp., escapes at (13) as soon as it opens on reaching the heat exchanger temperature of 280 - 300° C. Good mixing of the developing oil vapor or oil mist with the forced air takes place in the relatively short mixing volume between the valve (18) and the flame holder in the direction shown (29).

The second sketch shows a similar version of whisker heat exchanger in a flattened form. This version is still being tested, especially since it promises lower production costs. The following figure 13 shows the position of the whisker heat exchanger in the air supply pipe of a conventional oil burner at a scale of 1:1. The following two figures 14 and 15 show various types of indirectly-heated whisker heat exchangers where the first is a test model without control valve, and the following are the latest heat exchanger types with insulating shell and electromechanical control valves as well as a continuous temperature monitoring by means of an NTC resistance.

Fig. 12 Whisker heat exchanger with circular whisker network





According to patent drawing

Whisker heat exchanger with
flat whisker network (2-4 mm thick)

According to patent drawing	Whisker heat exchanger for flat whisker network (2-4 mm thick)

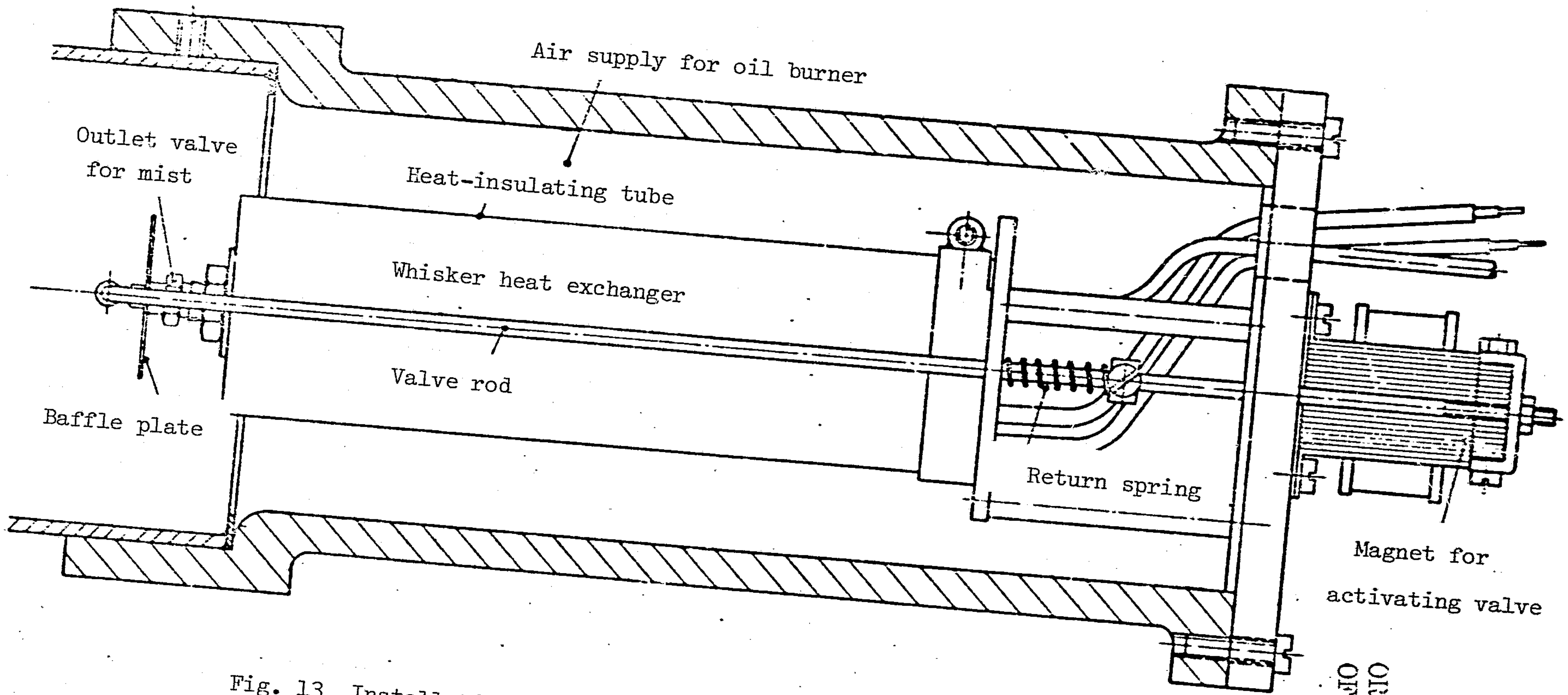


Fig. 13 Installation of whisker heat exchanger in a conventional oil burner replacing the atomizing nozzle.

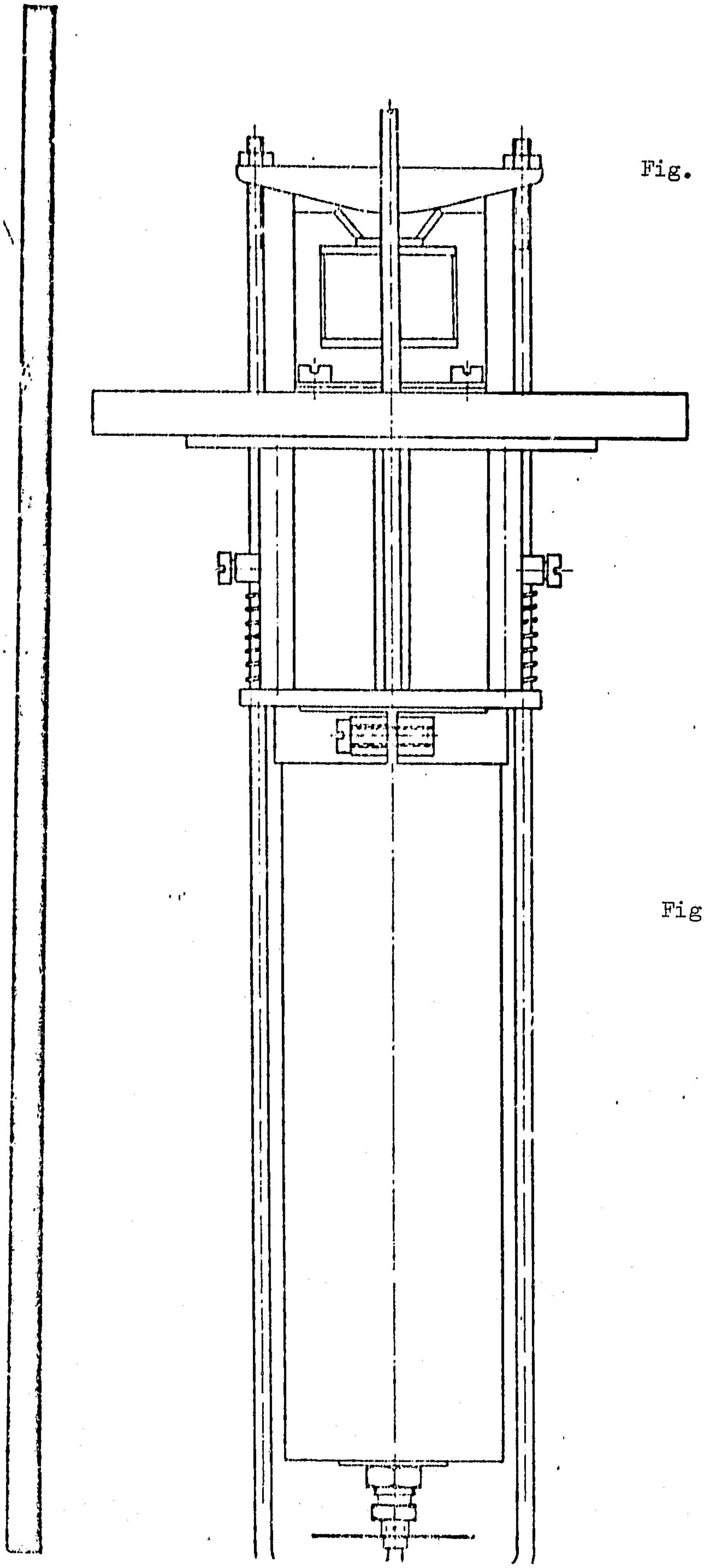


Fig. 14a

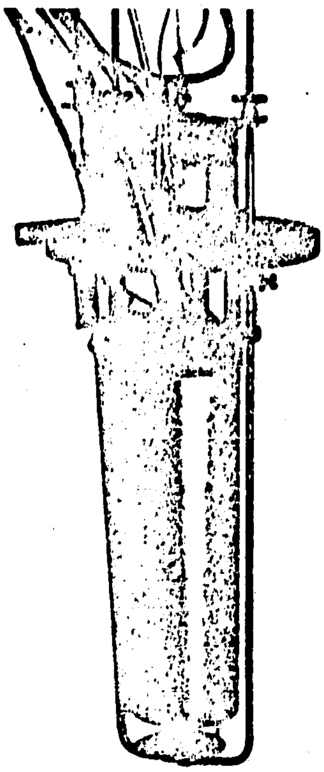


Fig. 14b

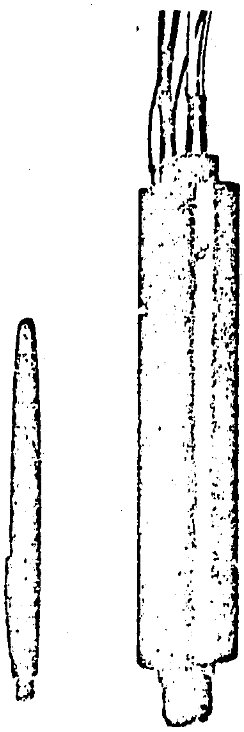
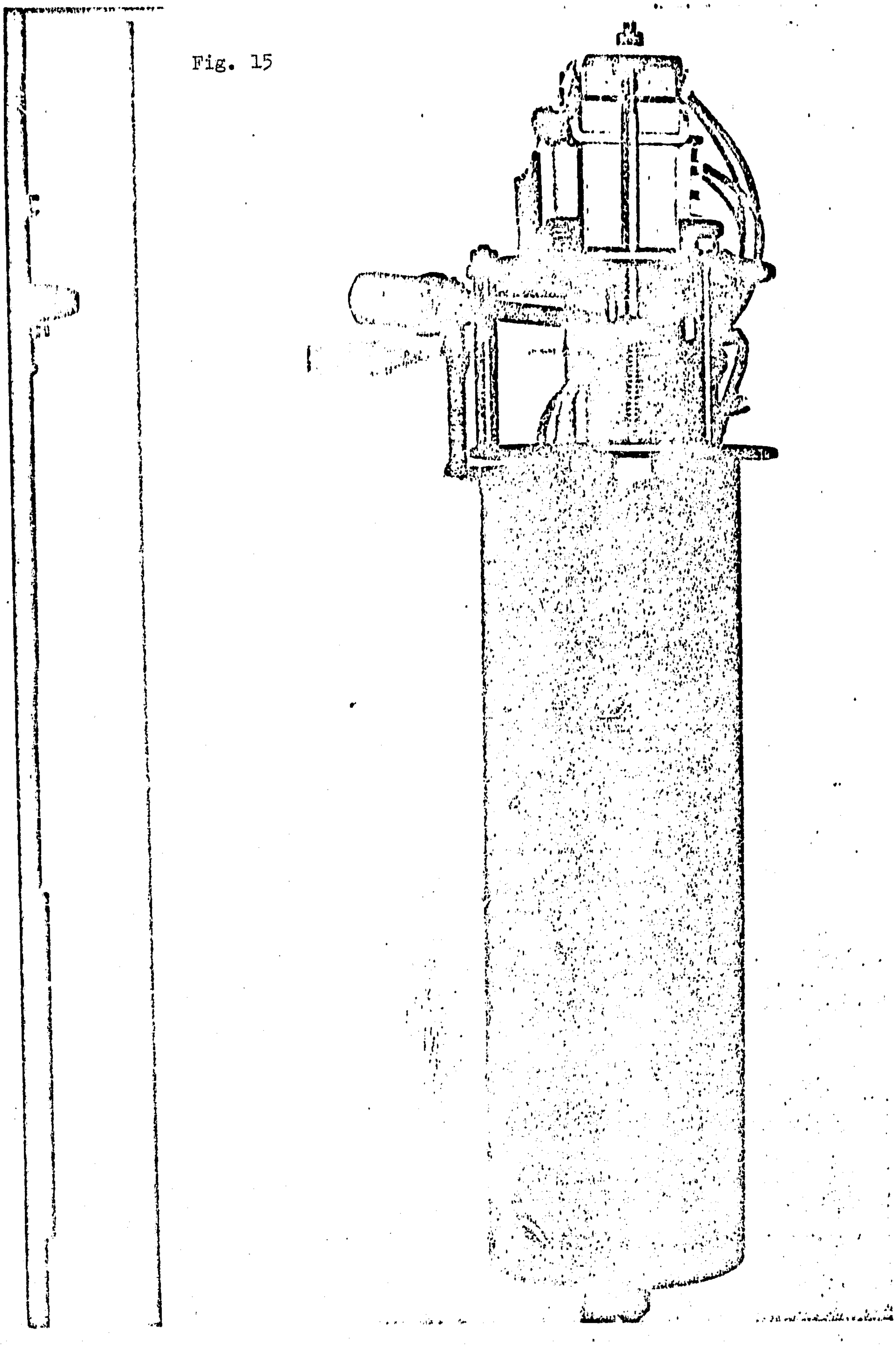


Fig. 15



The now following figure 16 represents a conventional oil burner which /56
is especially readily accessible by means of a cover over the flame tube. The whisker heat exchanger (tablet type) installed here can be readily seen. In this heat exchanger the amount of heating was controlled by a "Triac"; however, no controllable shut-off valve for the hot mist was used since the tests were of long duration with a continuously burning flame. Ignition was effected with only 5000 volts at the end of the flame tube, facing counterstream.

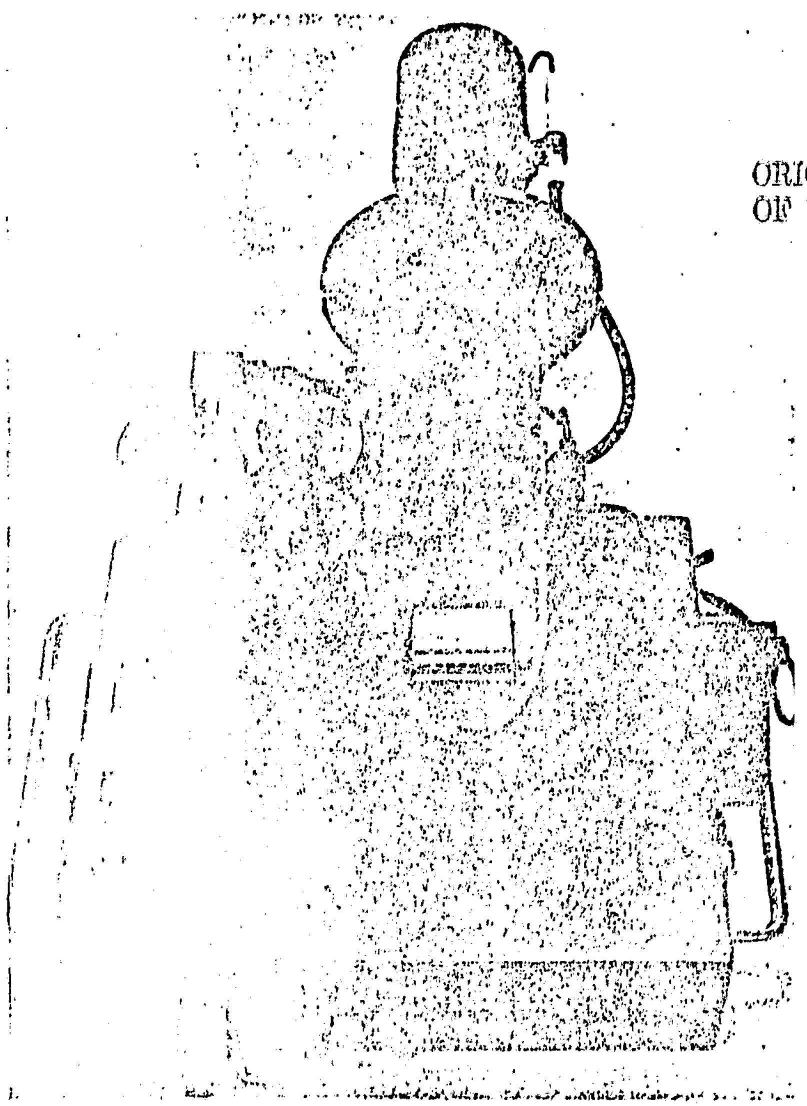


Figure 16

A hydraulic shut-off valve, controlled by heating oil pressure, was used in the heat exchanger (tablet type) shown in figure 17. /57

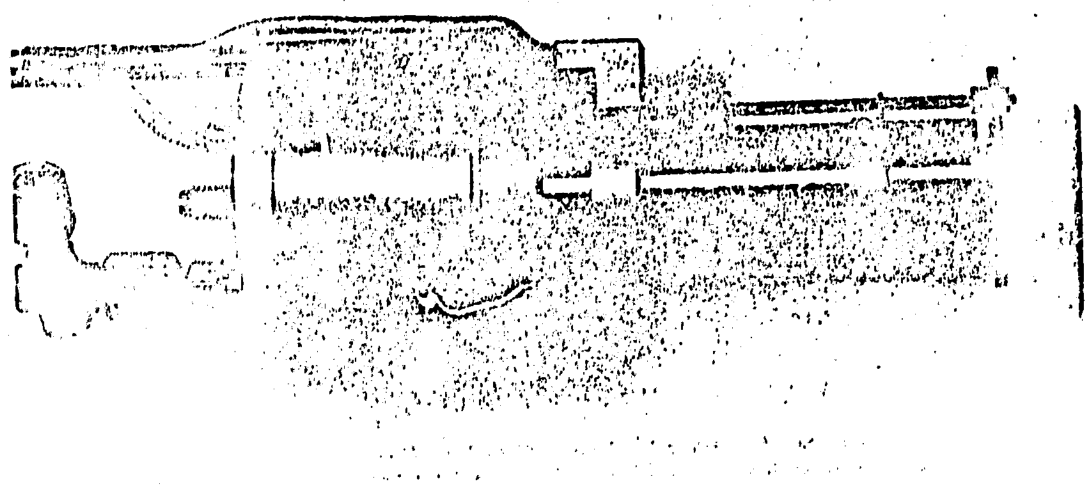


Figure 17

The next figure 18 shows an operational oil burner with a construction featuring tangential air supply where the whisker heat exchanger system can be easily inserted into the flame tube from the rear. A manometer in the oil supply tube monitors the pressure increase resulting from closing of the whisker pores. This whisker heat exchanger burner was also used for long-duration tests in connection with a conventional boiler and a complete radiator installation for the purpose of operating it under practical conditions. This complete heating installation was supplied to the oil burner industry for information purposes and to enable them to make their own measurements.

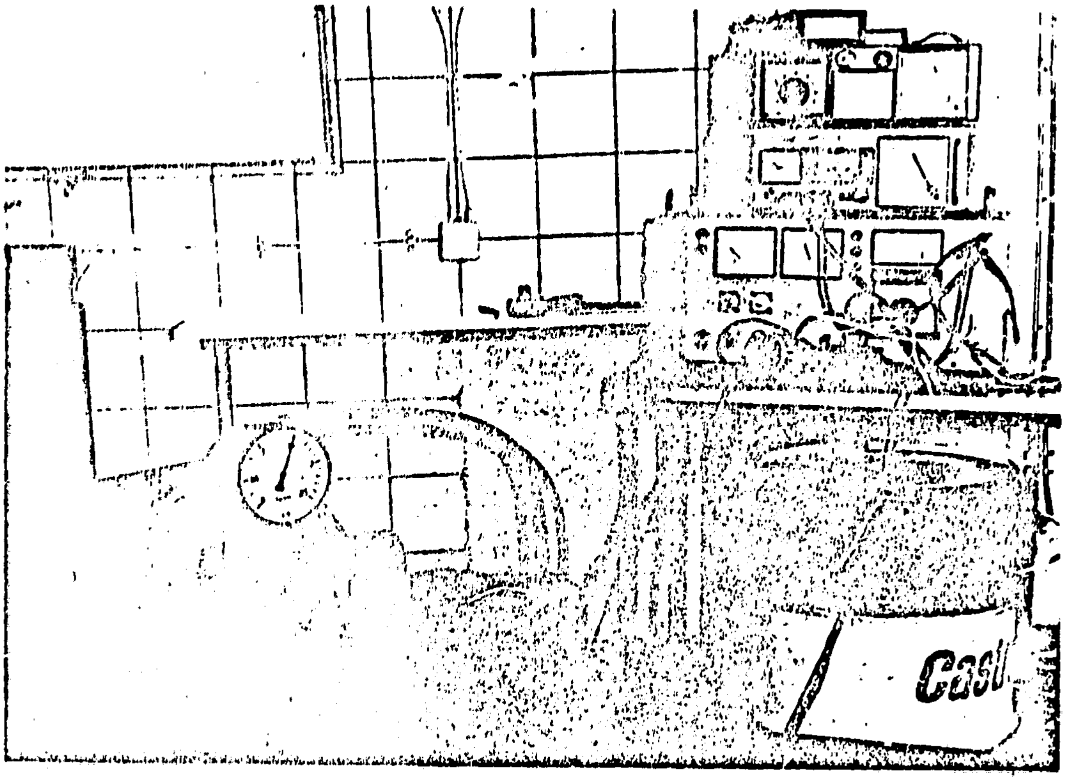


Figure 18

An additional modern construction of a conventional oil burner with whisker heat exchanger is shown in the next figure 19. Here the view is directly into the flame which is short and completely blue. However, it generates a long stream of hot combustion gases which serve to transfer convected heat to the boiler.

Figure 19

To demonstrate the operation of this oil burner with whisker heat exchanger the flame tube was removed, figure 20, so that one can clearly see the extremely fine and dense fog generated by the whisker heat exchanger. The fog exits with a temperature of about 300°C. It is clear that, as already shown in practice, one can convert a fog of such fine droplets, through suitable intensive mixing with air, into an ideal mixture which then, similar to that of a gas flame, burns with a blue flame and which, as desired, can be burned stoichiometrically or at other suitable fuel-air ratios. The flame is not particularly sensitive with regard to mixture control. Moreover, the flame is extraordinarily stable, aided by the fact that the combustion air is compressed, so that it is very difficult to blow it out. /59

Figure 20

ORIGINAL PAGE IS
OF POOR QUALITY

This oil burner was intended to demonstrate that a conventional oil burner with a normal flame tube can readily be converted to a functional and economical oil burner with low pollutant emission and with a constant blue flame. To date we have installed a sheet metal grate at the end of the flame tube which serves to give an especially good uniform flame. /60

This oil burner contains a whisker heat exchanger of the newest construction. This whisker heat exchanger is insulated very well thermally, is heated indirectly and is controlled electronically. Temperature monitoring at present is generally done with a NTC resistance; later on, however, it will be replaced by a simpler system of temperature control.

In addition the operation of the valve by means of an electromagnet is to be simplified in time, as well as the effective part of the whisker heat exchanger, i.e. the whisker column which will be made exchangeable as an inexpensive cartridge.

With regard to the safe operation of the whisker heat exchanger, it has been developed, with continuous improvements, to such a degree that we could ourselves start a limited-production fabrication. Up till now we have produced 100 heat exchangers of various types and made them operational. Here it was found that the performance values of the indirectly heated heat exchangers could be reproduced especially well after we had developed methods for classifying whisker sizes and for producing the whisker columns.

The finely divided oil mist which, in test and development efforts remains in the chamber for a long time unless it is ignited immediately, also produced some problems. It never ignited as a cloud, but it remained dangerous. It was not always possible to burn off the oil mist because it was first necessary /61
to study the shut-off valve of the heat exchanger, the production of the mist and the mixing with air. For this reason we pursued the opposite path, namely to again collect the mist by means of whisker skeleton and to condense it which normally is hardly possible with condensation devices. The following figure 21 shows a fog condensation device which is connected to a heat exchanger.

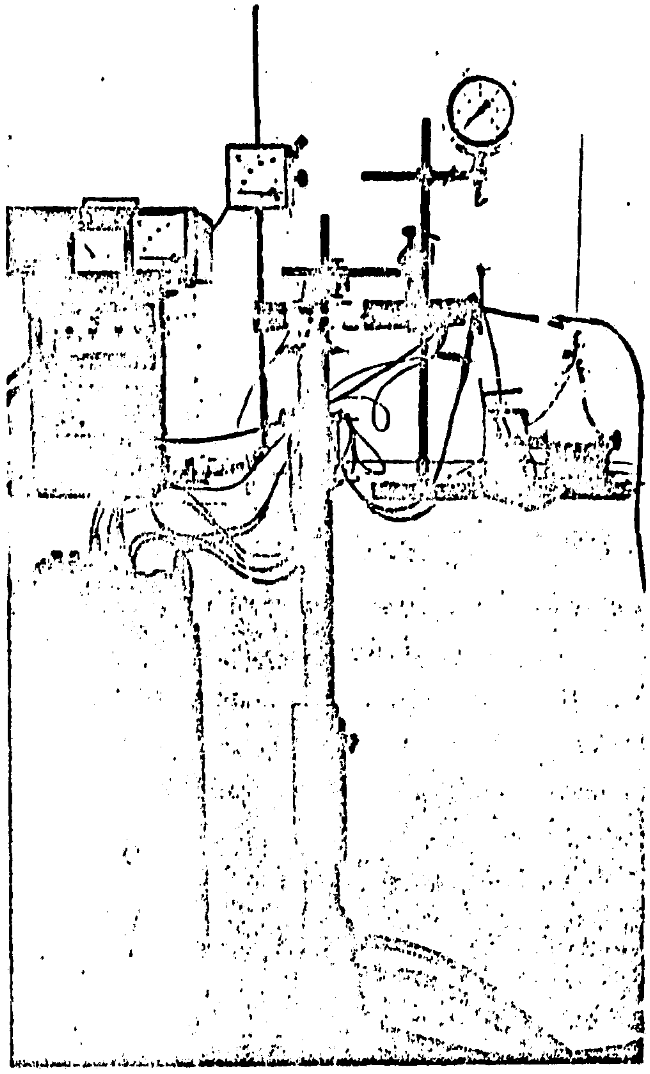


Figure 21

This condensation device consists essentially of a cooled, large, hollow /62
whisker column with circular cross section through which the fog flows radially from inside to outside, accompanied by suction air. Such a device makes it possible to test right in the work chamber, without danger of explosion and without polluting the air, the functional operation of the whisker heat exchanger without having to immediately burn the oil vapor or oil fog. Such a device is even more necessary for the no-less dangerous tests with gasoline rather than heating oil in which cases we have furnished absorption devices in larger sizes to the interested automobile industry.

The life of a whisker heat exchanger for preparing heating oil mixtures is very important in practical applications. As is well known, the light heating oil consists of various hydrocarbons, but also contains noticeably large amounts of water, air, organic sulfur compounds and sulfur acids and among the hydrocarbons many unsaturated compounds which are very reactive. Sulfur compounds and water probably will not attack the whisker skeleton greatly and one can protect himself against this. In any case, we have not yet observed a damaging reaction. It is a different case, however, with reactions between dissolved air and certain reactive hydrocarbons. At higher temperatures reactions take place in the whisker skeletons which lead to separation of fine aggregates which gradually can be deposited in the whisker cartridge. We have studied these reactions extensively and have determined that these separations occur especially often if the heating oil temperature is high enough that the higher-boiling fractions are vaporized and exposed to the air.

There are additives to the heating oil, however, which prevent the agglomeration of the particles separated from the oil to larger aggregates and which can delay the formation of such particles for longer times. Such additives are often used in automotive piston engines and were used by us. /63

Shown in the next two figures 22 and 23 are aggregations of the above discussed separation which were caused by vaporizing oil in the presence of air. Figure 23 shows a very small number of separation particles which were obtained under the same test conditions and which generally remained as individual particles and for hours did not ball together.

The life of the whisker skeletons as far as blockages by undesired separation particles are concerned, can thus be increased by additives to the oil which prevent the balling together of very fine separation particles and which pass these particles into the flame. Such additives are not the usual additives which are used for corrosion prevention or for reducing viscosity, but they are dispersion promoters.

Fig. 22

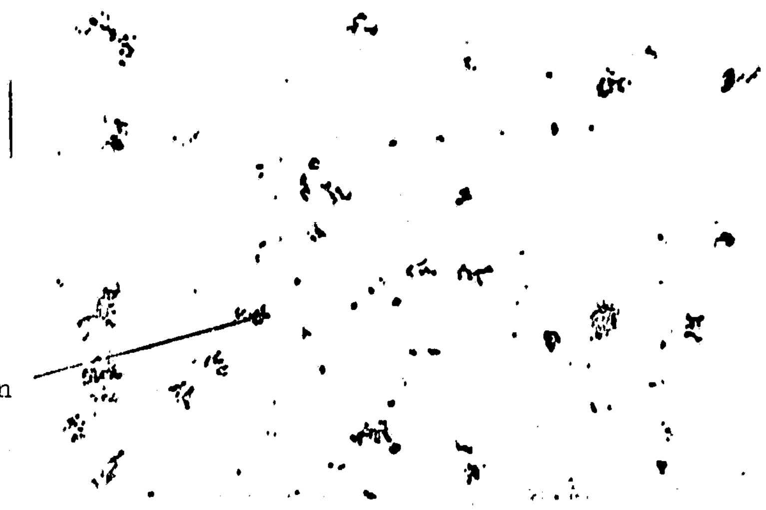
Black

Light brown

Dark brown

Fig. 23

Light brown



Figures 22 and 23

Summarizing results of the development /64

The development of special materials made from polycrystalline metal whiskers in the shape of pressure-resistant and highly porous fine networks has led to the creation of a new excellently efficient whisker heat exchanger. This whisker heat exchanger finds one of its most realistic and important areas of application in the preparation of heating oil for the purpose of technical control over a practical, complete combustion process.

This ideal combustion of heating oil made possible by the very fine misting of heating oil through the use of the whisker heat exchanger can, in an unusually effective and already industrially applicable manner, solve, in the future, one of the most predominant problems of energy conservation in the Federal Republic whereby, at the same time, the demands of environmental protection are pleasantly satisfied.

The clean blue flames resulting from combustion of oil utilizing the whisker heat exchanger are in contrast to all efforts made to date in this area which were concerned, above all, with methods of careful air introduction into the atomizing burner flame.

The use of whisker heat exchangers resulted in remarkable stability without the expenditure of excessive care measures and depends, to a much lesser degree than usual, on a careful tuning of the atomizer and air introduction system to the dimensions of the boiler.

The reproducibly good exhaust-gas concentrations are about 8-20 ppm CO, 15-15.5% CO_2 and a smoke number of zero. These values were determined by experts from the oil burner industry; similarly the overall efficiency of the entire heating cycle was calculated to be 93%.

The real overall efficiencies of conventional oil burner systems such as are in operation in Germany today, are often soberly quoted by experts to be /65 in the range of 40 - 70%. This does not contradict the fact that, with well-adjusted burners, efficiencies of 80 to 85% can be obtained.

However, since from our experience and in the judgment of oil burner manufacturers there is no reason to doubt the reliable maintaining of blue flames from whisker heat exchangers, one can also expect to maintain a high efficiency over long periods of time.

It has generally been estimated that an oil burner with a whisker heat exchanger saves, on the average, at least 15% of oil compared to a conventional burner. Since, at this time, there is no alternative in the Federal Republic for the problem of low-pollution combustion of heating oil which has been developed to the same degree as the whisker heat exchanger, it is appropriate to consider how much heating oil the whisker heat exchanger, in addition to improved environmental protection, can save based on the conversion or outright substitution of about 5 - 6 million operative burners of lower performance. We could here count on a very respectable saving of 5 - 6 million tons of heating oil per year. This does not take into account the savings that could be realized from industrial burners.

The oil burner industry, however, feels that it would be cheaper to install new oil burners with whisker heat exchangers than to retrofit the old systems with whisker heat exchangers.

According to our information it is not presumptious to assume that the oil burner with whisker heat exchangers could set the example for similar problems of low-pollution and oil-saving combustion in Europe and Japan. Furthermore, we know from personal experience of the conditions in the United States that the /66
development, which has been neglected for many years, must now be quickly resumed and accelerated and that there also is practically no alternative for the whisker heat exchanger in oil burners.

The use of heat exchangers in the oil burner industry is being directed and will undoubtedly soon extend, perforce, to the ever-increasing area of small burners of 11 kw/h and below, which, as is well known, can no longer be equipped with conventional atomizing burners. The urgency of this problem is still greater on an international scale; here, understandably, the superiority of oil preparation by means of whisker heat exchangers over that produced by atomization is readily demonstrated.

Here we can state with satisfaction that, within the framework of this report, it was only with the support of the Federal Republic that it was possible for us to solve so many difficult problems in such a short time which had arisen in the development of the whisker heat exchanger to its present status.

It goes without saying that we are on the way to still further simplification and cost reduction of the whisker heat exchanger or related systems; obviously industry is also making efforts to achieve very fine atomizations in other ways. The only thing that is important is the fact that finally a real potential with a high degree of technical maturity exists.

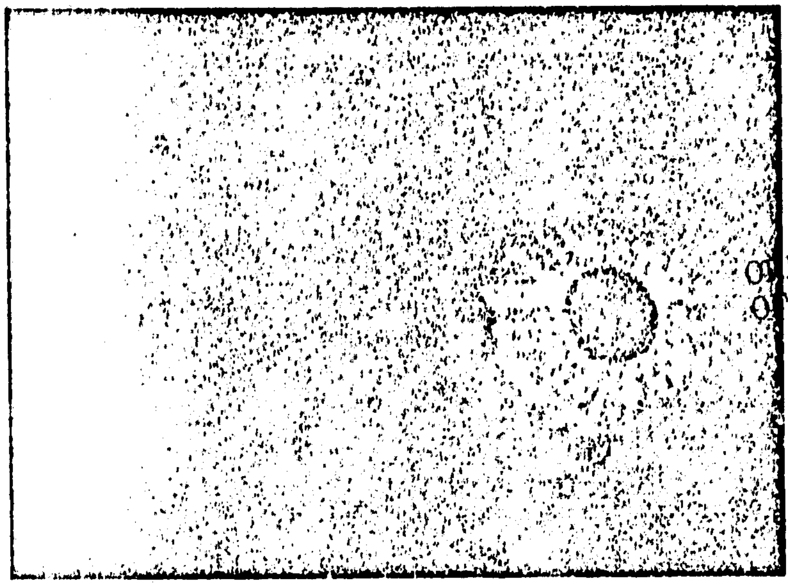


Figure 24 - Blue flame from heating oil achieved with whisker heat exchanger

As mentioned previously, an effective carburetion of gasoline for /68 automotive engines has always been a problem and, in the last few years, has become one of the most important development goals. From the beginning experts recognized the special effectiveness of whisker heat exchangers from polycrystalline whiskers, for there was no doubt as to how one had to proceed basically in theory to produce evaporators having large surfaces. It was therefore enlightening that whisker skeletons as contrasted to the state of the art, could go further than, for instance, porous products from sintered powder metal.

However, unlike the oil burner industry where everybody knew that a reproducible finer atomization of the oil droplets and the formation of a good mixture distribution would have to lead to improved combustion, there was no consensus of opinions in the evaluation of the degree of gasoline carburetion that was necessary.

The idea of fuel evaporation whose practical realization has often been attempted, comes to mind first when considering an idealized mixture preparation. Although the concept of fuel mist would be better suited to present-day engine construction, the term "mist" is a wide-ranging term and it is well known that mist-like atomized fuel can again be condensed in its way to the cylinder.

Thus many automotive manufacturers whom we supplied with whisker heat exchangers with controls, first experimented with vapors and, unfortunately, without much thought installed the whisker heat exchangers in commercial spray devices to which our heat exchangers could not be adapted without modification. An additional problem is the fact that the gasoline vapor can still condense in the suction tube on its way to the cylinder so that the gasoline vapor, prepared quickly and simply by the whisker heat exchanger could, in no way, guarantee /69
any appreciable progress in mixture preparation.

One of the most important German automobile firms, however, took pains to study, from the ground up, the operation of the whisker heat exchanger and to make use of its specific advantages. The whisker heat exchanger was actually used as we had intended, namely as a source of extremely fine mist formation. The drop sizes of the fog were rather uniform with a diameter of 2 - 4 microns. This drop size explains the extraordinarily great constancy of the gasoline mist which, as we had already determined in our own tests, hardly condensed on surfaces and also no more on the walls of the long tubes. The following figure 25 shows this very constant gasoline mist from a whisker heat exchanger nozzle. The heat exchanger was equipped with a valve which opened at 35 bar. In this case the gasoline was sprayed into the heat exchanger with a spray pump.

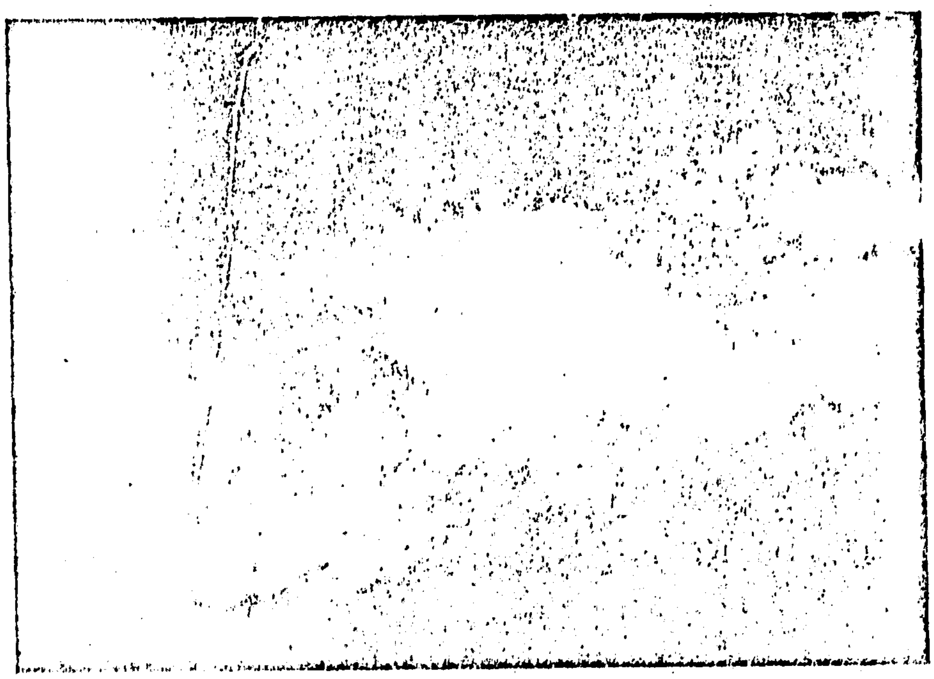


Figure 25

The continued investigation of the gasoline mist was conducted in a test /70 pipe which had many bends in order to study the behavior of the mist under difficult circumstances which never occur in the automotive engine.

Under such conditions the drops from a carburetor condense completely while the very fine mist droplets exited unharmed from the test pipe with a rate of 35%.

The following figure 26 shows a diagram of this experiment which already gave hints as to what could be determined in subsequent tests.

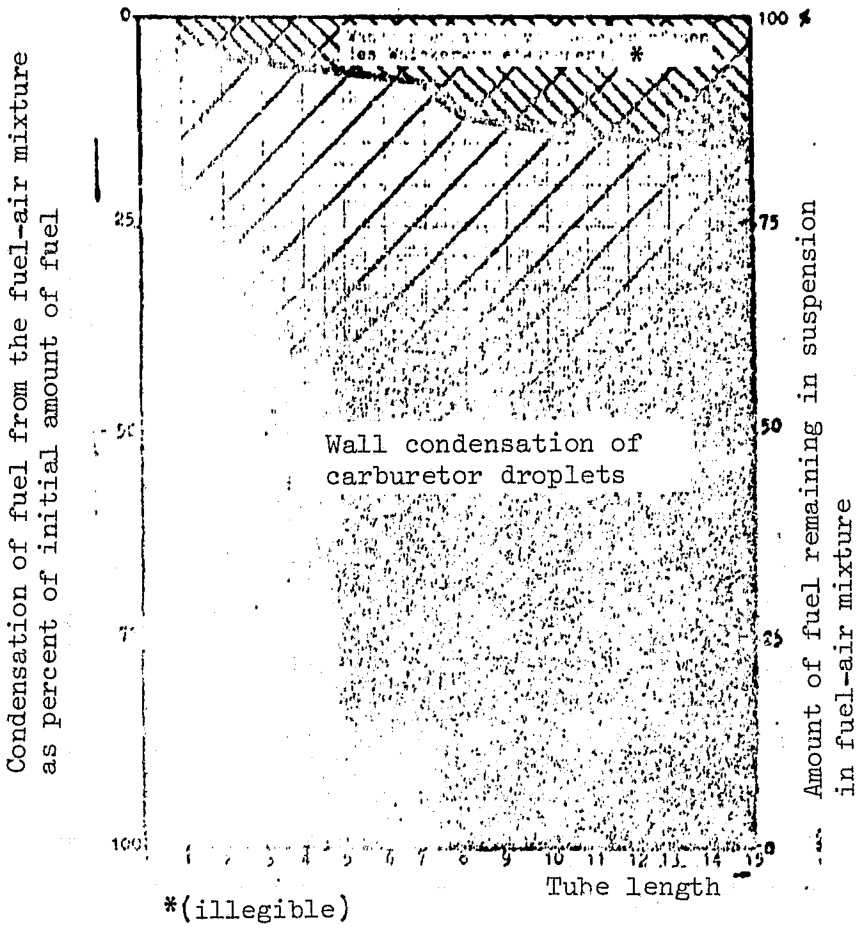


Figure 26 – Simulation of condensation of atomized or resp. fogged fuel in the suction tube under extremely difficult test conditions

Test conditions

Carburetor: entire fuel is condensed

Whisker heat exchanger: 86% of fuel remains suspended in fuel-air mixture

Such a fine mist as can be produced by a whisker heat exchanger, practically no longer condenses in the suction pipe thus finally offering a solution for one of the great problems, namely a uniform mixture supply to the various cylinders. /71

Another surprising experience was the fact that we were still able to ignite the mixture with a conventional spark plug at equivalence ratios of 1.6 to 1.7 instead of the expected value of 1.3.

It is not surprising that a measured saving of gasoline of 10 - 12% can be realized because of improved combustion and that in the future, as predicted by American experts, gasoline savings of 30 - 40% are in the realm of possibilities even for stratified charge engines using whisker heat exchangers.

There is no doubt that other automotive firms which have not yet been able to carry out these thorough preliminary investigations, will continue to study the use of whisker heat exchangers and that they will reach similar encouraging results. This gives us the opportunity to better adapt the continued development of the whisker heat exchanger for gasoline to the various engine problems of the future. Figure 27 shows the shape of the first successful model of a whisker heat exchanger for gasoline which was capable of producing fine gasoline mists at the rate of 28 kg/h.

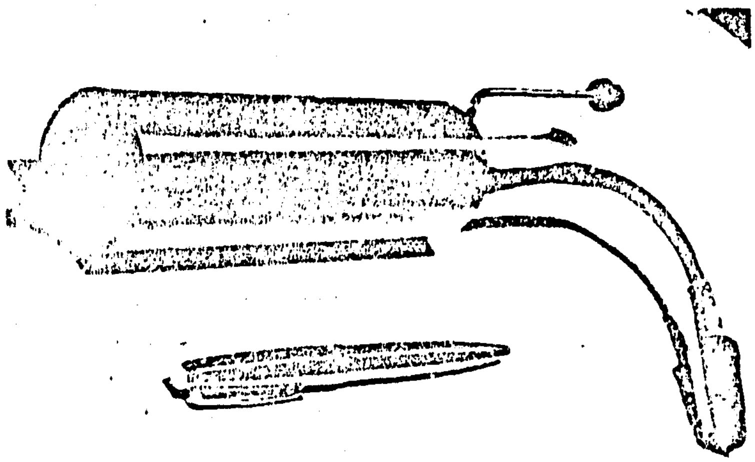


Figure 27

After these encouraging results with gasoline preparation we asked ourselves the question whether, in the future, we could develop modified ways for producing fine mists which could give a further reduction of the heat energy required for producing fine gasoline mists from the main fuel supply and which can cope with the problem of quick control. At the same time one had to keep in mind that the improvement of the mixture from conventional carburetors with the aid of whisker skeletons could be of great practical and economic interest. /72

During the study of the mechanical atomization and evaporation by whisker skeletons the following new points of view arose:

1) A whisker skeleton of fine pores with its high throughput of gaseous and liquid materials can produce gasoline mixtures of very fine droplets.

2) A whisker skeleton continuously covered with coarse gasoline droplets from the carburetor exposes such a large gasoline-covered surface to the combustion air flowing through that an appreciable part of the gasoline is carried off as an air-vapor mixture.

Both events, the breaking up into droplets and the evaporation by the whisker skeleton can be combined in that a large part of the gasoline entering the whisker skeleton is vaporized, and the remaining unvaporized portion is broken up into extremely fine liquid droplets by a suitably shaped exit layer of whiskers in the skeleton.

Tests of this type although not yet concluded demonstrate the remarkable advantages of this most simple, but effective method of fuel preparation. In this case the metallic structure of the whisker skeleton helps considerably to satisfy the requirements for heat addition since the heat of vaporization can be quickly transferred to the whiskers from the surroundings, or if need be, from an auxiliary heating source.

There is no more doubt today that the whisker heat exchanger can become a valuable addition to the possibilities for ideal fuel preparation. /73

Therefore we consider it worthwhile to take the second step in the development, along with the great experts of the automotive industry, to develop controllable whisker heat exchangers. At the same time we shall not ignore improvements in the functions of the carburetor since they not only offer a possibility to make the conventional carburetor constructively more effective, but also the possibility to improve considerably the effectiveness of carburetors of old design in order to, at least, provide for some savings in gasoline and in order to achieve cleaner exhaust gases. Such a development effort will also be conducted by us under the leadership of the present experts.