WADC TECHNICAL REPORT 55-255


# PRODUCTION OF METALLIZED FIBERS FOR DIPOLE CHAFF

*C. L. EMERSON, JR.*
*GEORGE E. NILES*

*EMERSON & CUMING, INC.*

*APRIL 1956*

MATERIALS LABORATORY
CONTRACT No. AF 33(616)-2604
PROJECT 4026

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
200 - June 1956

# FOREWORD

This report was prepared by Emerson & Cuming, Inc. under USAF Contract No. AF 33(616)-2604. This contract was initiated under Project No. 4026, "Development of Chaff Measuring Techniques and New Materials", Task No. 73697, "Development of New Chaff Materials, formerly RDO No. 107-48, "Equipment Jamming, Reflector-Type Radar, Dispersed from Aircraft", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. Ross Burrus acting as project engineer.

This report covers period of work from July 1, 1954 to June 30, 1955.

# ABSTRACT

The development of a metallized nylon fiber suitable for dipole chaff has been completed. The finished fiber is approximately 2.9 mils in diameter. It consists of a nylon monofilament 2.8 mils in diameter coated first with silver and then with nylon deposited from solvent. The electrical resistance is continuously less than 15 ohms/inch. Abrasion resistance and non-clumping is good. The cost of the packaged product is less than 0.01¢/foot of length.

## PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

TABLE OF CONTENTS

# LIST OF ILLUSTRATIONS

I

## SUMMARY

The development of a metallized synthetic monofilament meeting the requirements specified in Contract AF 33(616)-2604 have been successfully completed. Five million feet of a typical fiber have been produced, packaged and shipped to the Materials Laboratory, WADC.

The product has the following characteristics:

1. The synthetic monofilament is 2.8 mil nylon fiber, manufactured by E. I. DuPont, Wilmington, Delaware.

2. The metal coating is silver, deposited from #378 paint, manufactured by Handy & Harman, Inc., New York City, approximately 0.002 gms./foot of fiber.

3. The overcoat is nylon, less than 0.0001" thick.

4. The electrical resistance is continuously less than 15 ohms/in. on over ninety percent of the fiber.

5. Abrasion resistance to flaking of silver is good, this being provided by the overcoat.

6. Clumping or sticking together of fibers is less than that of the bare monofilament. It is substantially the same as silvered monofilament without overcoat.

The process is very simple. Nylon, on one pound bobbins, is coned to produce 1/4 pound cardboard cones each holding 83,000 feet of monofilament. The nylon monofilament is passed continuously through the following treatment:

1. A silver dip tank containing 57% silver by weight dispersed in butyl cellosolve.

2. An aluminum box infra-red dryer operated at 220°C wall temperature with a retention time of thirty seconds.

3. A nylon dip tank containing 2.5% by weight nylon dissolved in ethyl alcohol and dyed red.

4. An aluminum box infra-red dryer operated at 130°C wall temperature with a retention time of 30 seconds.

5. Windup on a four spoke reel, 100,000 feet per reel.

6. Removal and packaging in a 12" x 1" x 1-1/2" cellulose acetate container holding 100,000 ends.

Tension on the fibers is maintained by an appropriate device at the feed cone. This prevents twisting prior to packaging. The package is readily sliced with a sharp friction blade bandsaw.

The equipment while custom built is fabricated from standard commercial elements and is readily reproduced and/or expanded.

Since silver is applied in a dip operation its utilization is essentially 100%. Material cost of the packaged product is approximately $100/million feet.

II

## RESULTS

The results of this work are most adequately revealed by the 5,000,000 feet of material produced and delivered to WADC. The characteristics of this product are:

1. A basic 2.8 mil diameter nylon monofilament of high tensile strength and excellent durability. It has a high heat distortion point and a high degree of chemical inertness.

2. This fiber is continuously coated with silver to a weight of 0.002 gms./ft. resulting in a surface resistance of approximately 10 ohms/in.

3. The silvered fiber is overcoated with a very thin nylon film to enhance corrosion and abrasion resistance, and to enhance rigidity.

4. The finished fiber is packed in rectangular tubular cellulose acetate containers 1" x 1-1/2" x 12" in length. This package is readily sliced by means of a sharp friction bandsaw.

The major conditions existing during most of the 5,000,000 foot run are as follows:

1. Input: 78 parallel nylon monofilaments, spaced equally across a 10" width.

2. Speed: 7.5 feet per minute; 850,000 feet per day.

3. Temperatures: 220$^{\circ}$C wall temperature in silver dryer; 130$^{\circ}$ C. in nylon dryer.

4. Resistance: 10 ohms/in.; 0.002 grams silver per foot of monofilament.

5. Product Take Off: Change reels each 100,000 feet of product.

6. Secondary conditions:
   - a. Continuous agitation (by Synthron vibrator) of silver dip tank.
   - b. Continuous Teflon doctoring of coated fibers.
   - 3. Continuous resistance reading of selected fibers.

Material costs are approximately $100 per million feet of product.

Curves correlating:

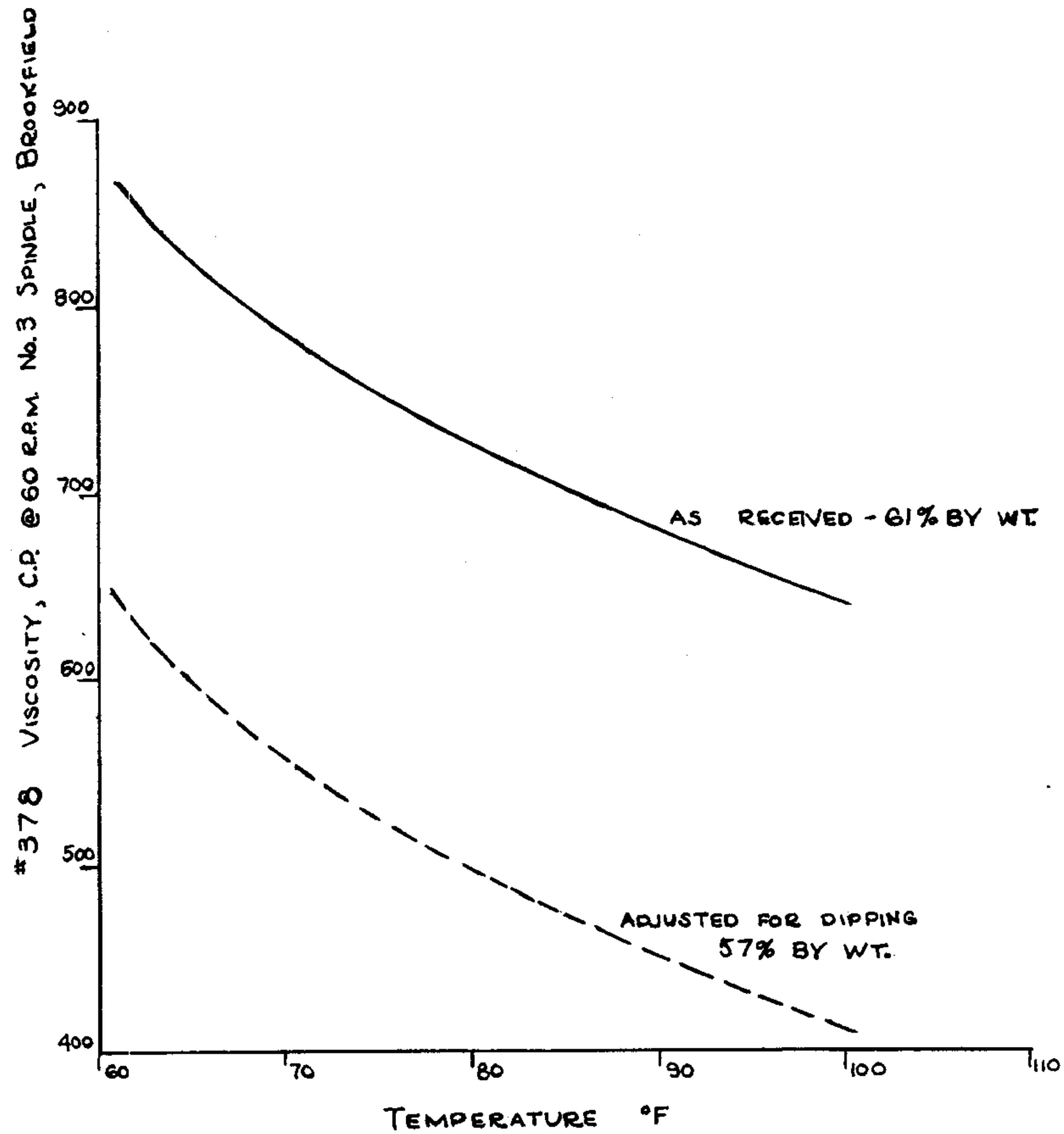
1. Silver dispersion viscosity to temperature.

2. Viscosity to amount of silver deposited at variable speed.

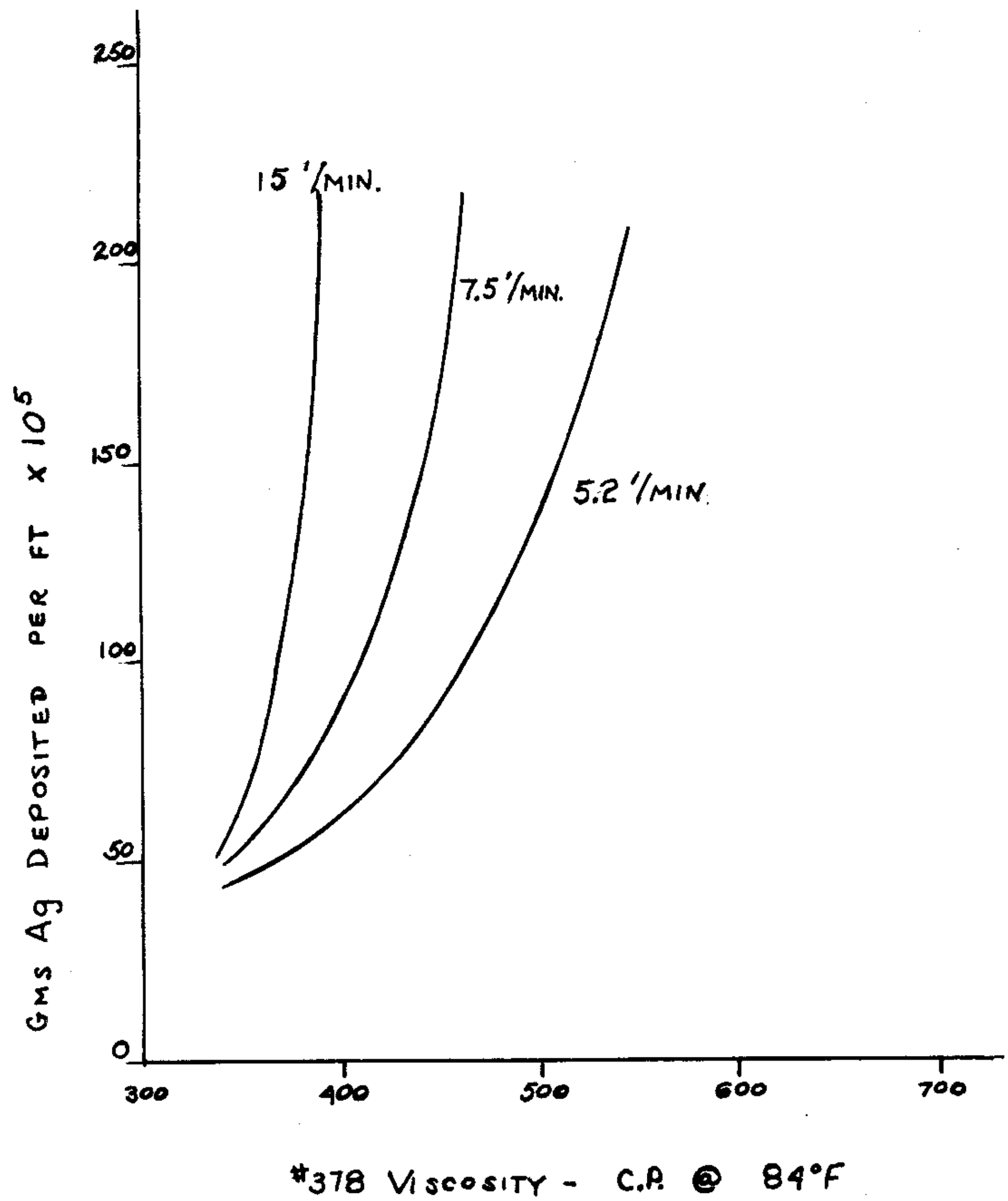
and 3. Amount of silver deposited to resistance of the coated fiber in ohms/in. of length.

are shown in Figs. 1, 2, and 3.

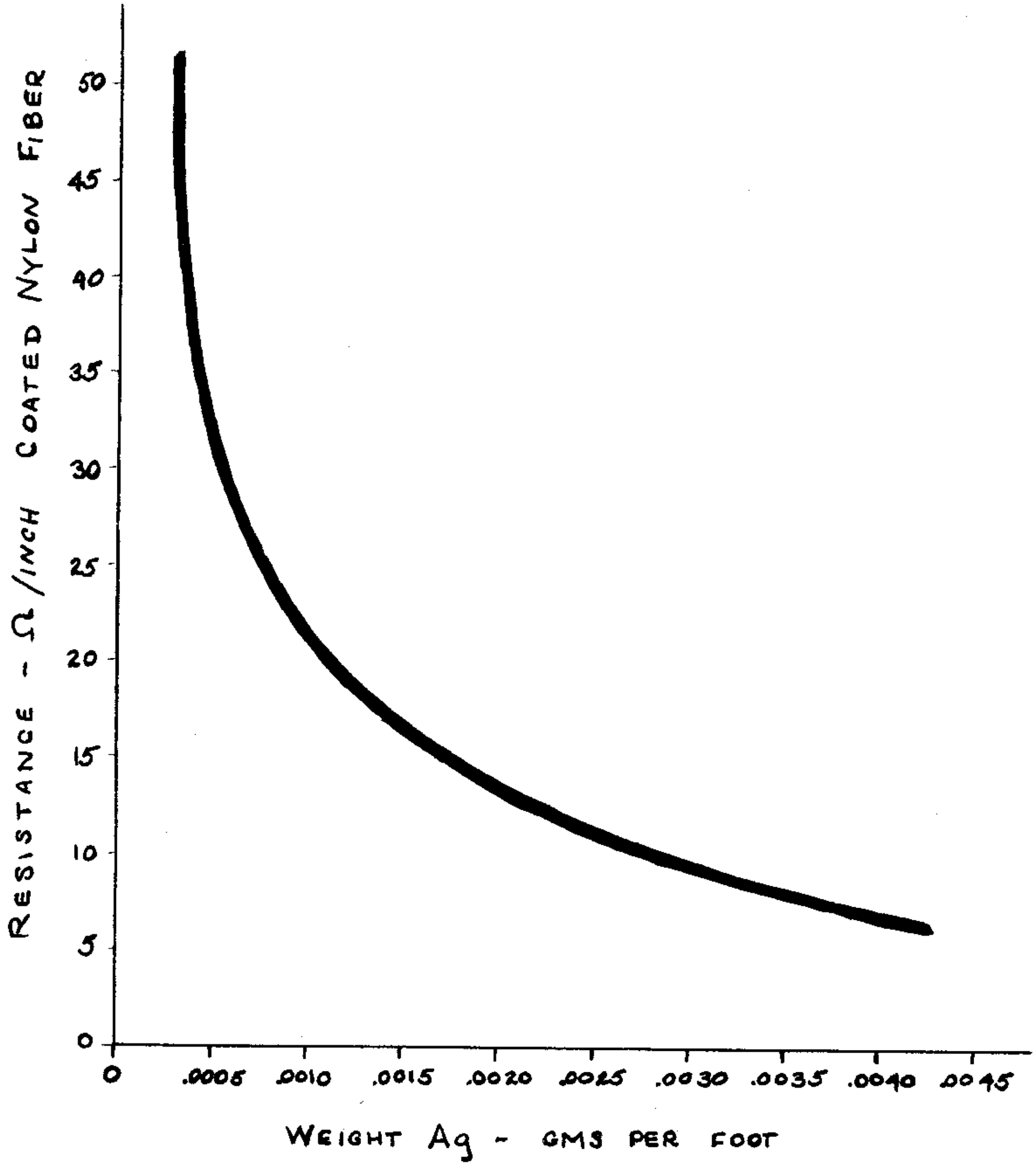
The equipment developed for the job is very simple. While custom built it is composed of readily available commercial items and can be expanded easily at low cost. Aside from engineering design work, a similar machine to produce 50, 000, 000 feet per day would probably not exceed $20, 000 in total construction cost.




| | |
|---|---|
| FIG 1: SILVER DISPERSION VISCOSITY VS TEMPERATURE | SCALE |
| | ACCT. WADC AF33(616)2604 |
| | NO. |




| | |
|---|---|
| FIG 2: GRAMS SILVER DEPOSITED VS. SILVER DISPERSION VISCOSITY | SCALE |
| | ACCT. WADC AF33(616)2604 |
| | NO. |




| FIG 3 ELECTRICAL RESISTANCE VS. GRAMS SILVER DEPOSITED | SCALE |
|---|---|
| | ACCT. WADC AF33(616)2604 |
| | NO. |

# III

## DISCUSSION

### Raw Materials

a. Fiber

Early exploration into the availability of various types of synthetic monofilaments indicated that nylon was the only one meeting the 0.003" ± 0.001" requirement on diameter. It is available in quantity as a 2.8 mil fiber. It was chosen for this reason as the basic raw material. The nylon fiber has high tensile strength, is chemically inert, and has a high heat distortion point. For these reasons it is also an excellent choice.

Cost of the nylon in quantity is $4.25/pound. One pound contains 333,000 feet. Thus, its cost is $ 12.75/million feet.

Saran and Polystyrene are available as 0.005" and 0.007" diameter fibers respectively. Neither is as strong, chemically inert or low cost as nylon.

b. Metal Coating

Previous experience with deposition of silver on plastic materials, in particular, plastic film, led to its use in initial experimentation. Silver coatings, deposited chemically, were thin, dense, highly conductive and had good adhesion.

Early fiber samples coated by depositing silver chemically were entirely successful in meeting the resistance specification of 100 ohms/in. As a matter of fact, samples were made showing 1, 2, and 3 ohms/in. surface resistance.

Silver utilization, however, was poor being in the neighborhood of 5%. This meant the necessity for developing a silver recovery and recycle system. Ageing characteristics were also questionable due to oxidation of the thin silver coat. Consequently, other experiments were carried out with various silver deposition methods. It was found possible to dip coat the monofilament by repeated application of silver paint. DuPont silver lacquer No. 4817 and Handy & Harman No. 340 were tried. The number of dips required was 15 to reach 20 ohm/in. resistance range.

Finally, experimentation with silver dispersion No. 378 of Handy & Harman, Inc. made it possible to apply a good coat in one dip. Rather close control of solids content and viscosity is required. The exceptionally small particle size of the silver, 1-2 microns, is chiefly responsible for its outstanding success.

When adjusted to 57% ± 0.5% solids content and 450 ± 30 centipoises viscosity, the No. 378 silver is capable of depositing a continuous film on a single pass of the fiber. Rate of throughput of the fiber will then determine surface resistance in ohms/in. At a deposition of 0.002 gms/ft. the resistance is continuously less than 15 ohms/in. This material was, therefore, adopted for use.

It is interesting to note the close correlation between the shape of the experimentally determined curve of Fig. 3, Page 7 and the corresponding curve based upon the relationship, Resistance $\propto \frac{1}{\text{Wt. Ag}}$

The curve of Fig. 3 is based upon 17 points obtained by weighing, in each case, the silver deposited upon fifty feet of fiber, the weighing, being itself accurate to 0.0001 gms produces an accuracy in a given point varying from 1 part in 2000 to 5 parts in 200.. The correlation is excellent.

c. Overcoat

The most desirable overcoat for the silver should provide

1. Corrosion protection
2. Abrasion resistance
3. Humidity protection
4. Freedom from sticking or clumping
5. Increased rigidity

Many materials were tried each with its limitations until work with soluble nylon showed it to be very good in almost all respects. A 2.5% concentration in ethyl alcohol was found best. Beading of the nylon overcoat was severe in 20 and 10% concentration, whereas 5%, although smooth, resulted in a product which clumped due to the fibers being sticky. While not an electrical insulator due to its extreme thinness, the 2.5% coat provides the above listed characteristics. It deposits in a smooth continuous film of considerable toughness. In this work it was dyed to red for purposes of observation.

d. Costs

Basis: 1,000,000 feet of nylon monofilament

| | | |
|---|---|---|
| Nylon | @ $4.25/lb | $12.75 |
| Silver | @ 0.002 gms/ft.; $1.32/troy oz. | 85.00 |
| Nylon overcoat | | 5.00 |
| Total material cost | | $ 102.75 |

This represents a cost of about 0.01¢ per foot. The silver deposition can be reduced approximately in one-half lowering total material cost to about 60% of this figure. Under these conditions dipole resistance will measure approximately 20 ohms/in. of length.

Process

The process consists basically of depositing silver from a viscous dispersion in solvent onto a continuously moving fiber, then heating the coated fiber, while under tension, to near its softening point in order to achieve the maximum adhesion of the silver.

The silvered fiber is then passed continuously through a second dip tank wherein it picks up a thin protective coat of nylon. This is deposited from a 2.5% solution of Zytel (soluble nylon, E. I. DuPont) in ethyl alcohol. The nylon fiber is dried and the resulting silvered and coated monofilament is wound upon a four spoke reel.

Individual packages containing 100,000 ends are cut from the reel and packed in a rectangular tube of performed cellulose acetate 1" x 1-1/2" x 12" in length.

The outstanding merits of this process are its basic simplicity and its 100% utilization of silver.

Nylon monofilaments must be handled very carefully. Electrostatic attraction can be a serious nuisance until after the silvering has been achieved. Only by spacing the fibers laterally no closer than 1/8" was it possible to operate the machine continuously without twisting together of the fibers. This process utilizes an easily handled 1/4 pound cone containing approximately 83,000 feet of monofilament. Consequently, a number of fibers is fed simultaneously into the silvering machine. The maximum number of parallel fibers which can be handled with present equipment is eighty (80), or eight (8) per inch across the 10" width.

a. Conditions of process

1. Parallel fibers fed from 1/4 pound cones, under tension.

2. Silver dip tank under continuous agitation.

   a. Silver concentration 57.0 $\pm$ 0.5% in butyl cellusolve.

   b. Viscosity, Brookfield, 450 cps at 70°F.

3. Infra-red silver coating dryer operated at 220°C.

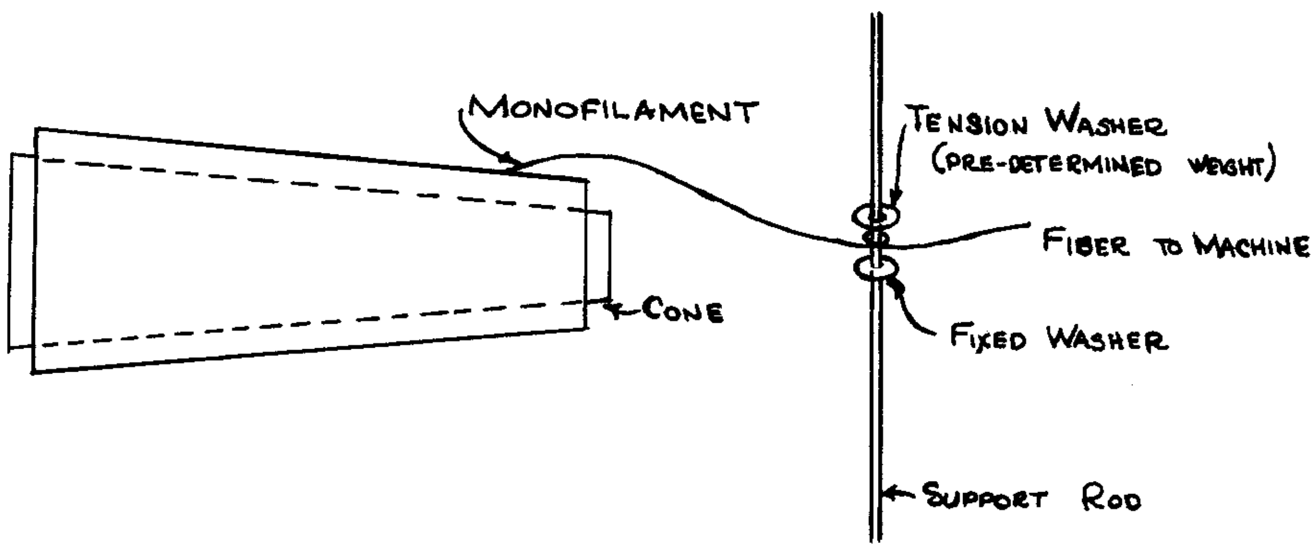
4. Nylon dip tank containing 2.3% Zytel in ethyl alcohol.

5. Infra-red nylon coating dryer operated at 130°C.

6. Four spoke windup reel, tension being maintained from feed off spot at nylon cone.

Equipment

Considerable work was required to develop a reliable mechanical handling system for the monofilaments. Adequate maintenance of tension on a single fiber was finally achieved by use of a simple washer device.




This coupled with helical steel spring combs located before, after and in the dip tanks solved the problem of preventing twisting prior to windup.

Solvent evaporation after silver deposition was a small consideration, since the silver dispersion was so concentrated. Good control was required, however, to soften the nylon fiber without breaking it since it was under tension. Standard Chromalox, infra-red heaters were found to be entirely satisfactory when operated by proportional timers.

This drying system was extended to the nylon overcoat, operating at a lower temperature. Three parallel 2500 watt, 240 volt heaters, enclosed in an aluminum box 1' x 1' x 4', were used in each case.

Continuous agitation of the silver dispersion was found very beneficial during the 5,000,000 foot run and was achieved by use of a Syntron Vibrator, Model V-15 operating on 110v at 60 cy, 3600 vibrations/min. This operation was established after the first 400,000 feet of product had been made. A considerable improvement in uniformity of resistance per inch of fiber and from fiber to fiber was made possible. No agitation was required in the nylon dip tank.

A Veeder-Root counter for measuring take-off footage completed the basic equipment.

The entire system was powered by a 1/2 HP motor reduced through a gear head to 36 rpm. The various sprokets were connected by chain linkages.

Fig. 4, is a flow sheet showing the equipment layout and major process conditions.


FIG. 4: PROCESS FLOW SHEET FOR SILVERING 40 DENIER NYLON MONOFILAMENT
5-21-55
CONTRACT NO. AF 33(616)-2604

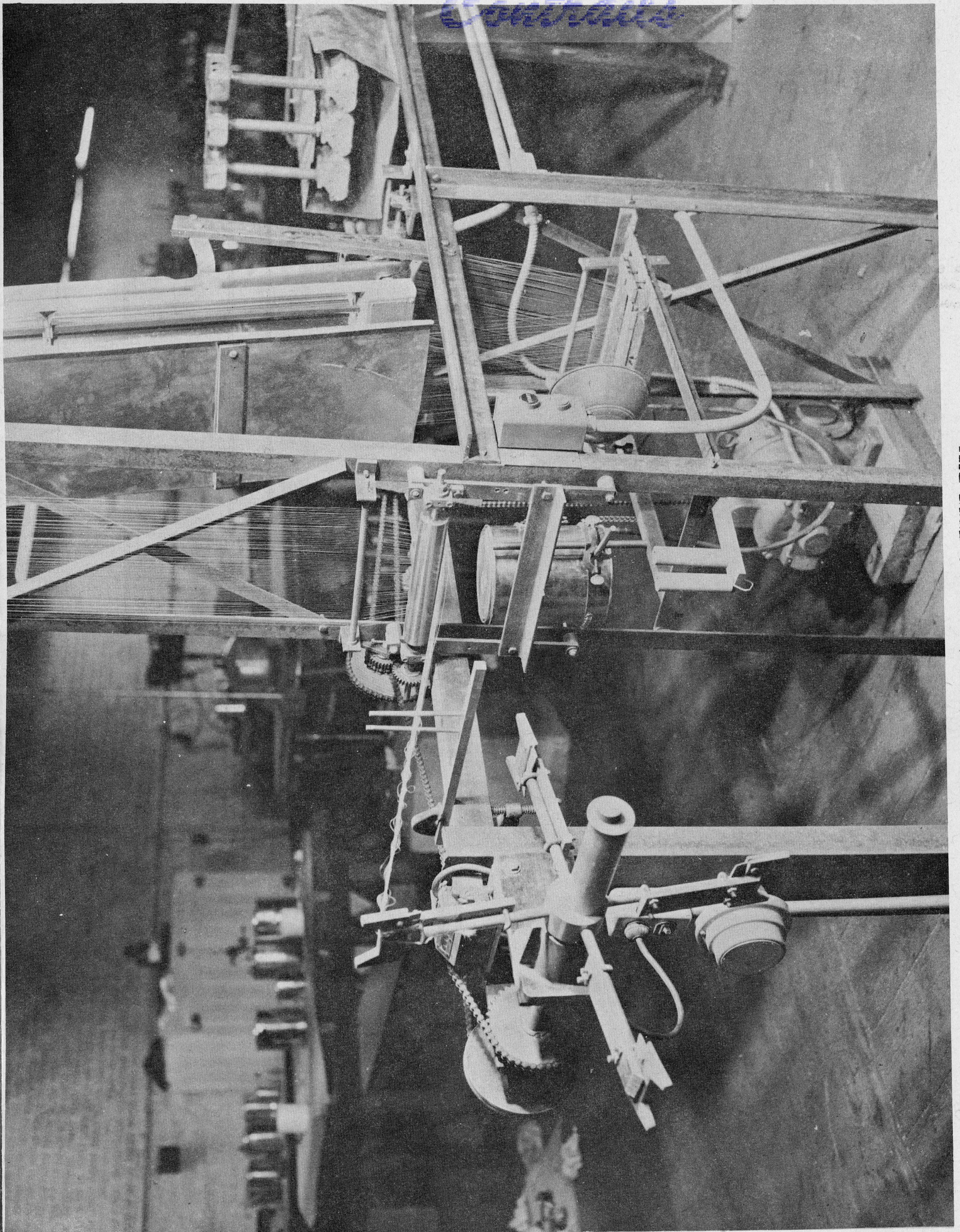


FIGURE 5. MACHINE DURING 5,000,000 FEET RUN

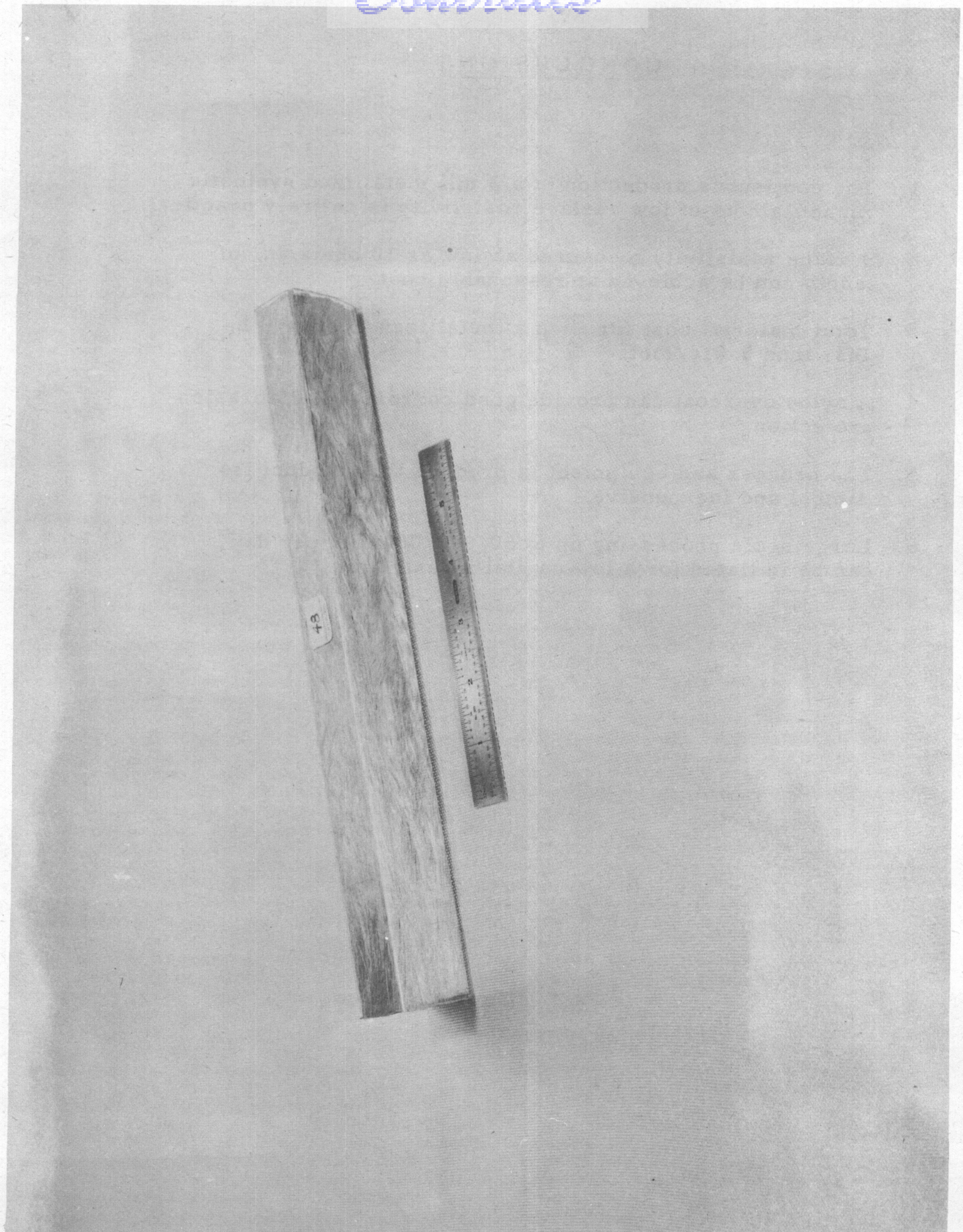


FIGURE 6. PRODUCTION PACKAGE

IV

## CONCLUSIONS

1. The continuous production of a 3 mil metallized synthetic monofilament of low surface resistivity is entirely practical.
2. Surface resistivity measured as low as 10 ohms/in. of length can be achieved at reasonable cost.
3. Total material cost for such a metallized fiber will be less than 0.01¢/foot.
4. A nylon overcoat can provide good corrosion and abrasion protection.
5. The process and equipment to produce this product is simple and inexpensive.
6. Large scale processing up to 50,000,000 feet per day can be initiated for a low capital investment.

# V APPENDIX

A. This section of the Appendix to WADC Technical Report 55-255 is concerned with a description of the chemical silvering process and equipment used to produce early metallized fiber samples under Contract AF 33(616)-2604.

This process is proprietary with Emerson & Cuming, Inc. and patent has been applied for.

The Process:

This continuous chemical process for silvering plastic film and fibers can be divided into the following basic steps:

1) Pretreatment of the plastic in hot 17 - 1/2% NaOH.

2) Washing and treatment with tin chloride solution.

3) Washing and silvering.

4) Final washing and drying.

Each part of this process is described in turn below.

1) Plastic Pretreatment

As received, the surface of the plastic, for example, polyester film, is quite hydrophobic, being essentially non-wettable by water and water solutions. In this state, the film cannot be satisfactorily silvered by chemical techniques. It has been found that the surface of the film can be rendered hydrophilic by boiling in 17 - 20% sodium hydroxide for about two minutes.

This strong caustic treatment saponifies some of the ester linkages on the surface of the foil:

$$R\text{-}\overset{=O}{C}\text{-}O\text{-}C\text{-}R' \longrightarrow R\text{-}\overset{=O}{C}\text{-}ONa + R'\text{-}\underset{H}{\overset{H}{C}}\text{-}OH$$

which resulting groups are quite hydrophilic. It is not necessary to saponify all of the surface ester linkage to radically change the wetting characteristics of the plastic film.

It will become apparent in the following sections that there is a strong possibility that the adhesion of the metal to the plastic film materially benefits by this surface treatment through the medium of ion exchange.

2) Tin Chloride Treatment

After the caustic soda has been washed off, the plastic film can be silvered. Experimental results indicate, however, that a somewhat more adherent silver layer can be had if the now hydrophilic plastic film is first treated with a 1 - 5% suspension of stannous chloride. Times, temperatures, and tin chloride concentration do not appear to be critical as the effect appears to reach its maximum almost instantaneously. It is important to thoroughly wash the film to remove all unreacted tin chloride so that the silvering solution is not unduly destabilized.

3) Silvering

The continuous silvering process is as follows:

To a 1-1/3% silver nitrate solution is added sufficient 10% caustic either soda or potash, to make the resulting solution 1% in silver nitrate. Immediately a dense, brown precipitate is formed. This precipitate is dissolved by the slow addition of 29% ammonium hydroxide, stirring and gentle heating not in excess of 45°C. Care must be taken to stir for a long enough time between ammonia additions so that the minimum amount can be used. To this solution is now added, very carefully, small amounts of 7% solution of silver nitrate until a small amount of dark brown precipitate forms, which does not redissolve. This suspension is filtered, and the filtered solution is now suitable for the silvering operation.

To reduce the silver-ammonia complex to metallic silver, use is made of such mild agents as reducing sugars, formaldehyde, etc. In this process, a 7-1/2% solution of dextrose has been prepared by boiling the proper quantities of dextrose and water and cooling for use.

Four volume of silver solution and one volume of sugar solution are heated separately to 32°C., rapidly mixed and in ten seconds or less flowed over the wet Mylar Film. Two minutes at 32°C., is sufficient to produce a fine mirror with a minimum of dark brown surface smut, which is presumable silver oxide. Times in excess of two minutes lead to the formation of an excess of this smut, which is not completely removed by washing. This oxide film does not appear to harm the electrical conductivity of the silvered film.

4) Final Washing and Drying

Drying is comparatively simple and a satisfactory result can be had by convention drying or infra-red radiation drying. It appears that the adhesion of the silver to the plastic foil is enhanced when temperatures of 330-350°F. are used. This may be due to a softening of the plastic film and to the slight diffusion of the silver into the surface of the film.

The Equipment

Continuous pilot equipment to carry out the above process is illustrated in the attached photo plate No. 7. Some of the various items are as follows:

1) Caustic tank with strip heaters below. This is the first stage of the equipment. The film or fiber makes six (6) horizontal passes through the liquor before emerging.

2) Spray wash to remove caustic from treated plastic.

3) Tin Chloride tank; also six horizontal passes.

4) Spray wash for tin chloride, treated plastic.

5) Sugar solution tank.

6) Silver nitrate tank.

7) Mixing nozzle to deposit silver nitrate and reducing sugars on moving plastics.

8) Depositing trough - 20' long. Here the precipitated silver deposits on continuously moving plastic as it moves along with it. Pitch is adjustable to allow for processing various types of plastics materials.

9) One of three bank of infra-red heater sections - three sections are in series and are individually controlled from electrical panel board partially seen in right hand corner of photo.

10) Product windup roll-driven as shown with friction clutch to regulate tension.

This equipment is capable of silvering plastic film and fiber at rates of 20 feet per minute. It can handle film up to 6" in width or several hundred fibers in parallel.

Photos showing the basic elements of the equipment are attached.

| Plate No. | Description |
|---|---|
| 7 | Chemical treating tanks. |
| 8 | Feed assembly showing a few feed cones. |
| 9 | Spray wash and blower drier. |
| 10 | Lacquer coating tank and windup reel. |

While the process described above for polyester film was adapted without change to nylon film it worked very well. Thickness increase was not measurable with a micrometer and resistances were 3 ohms/in. and lower.

Silver utilization was very poor, however, with this equipment and funds were not available to work out a complete silver recycle system. Consequently, work emphasis was shifted to methods which would insure good utilization of silver in a simple process. The results of this work are given in the main section of this report.

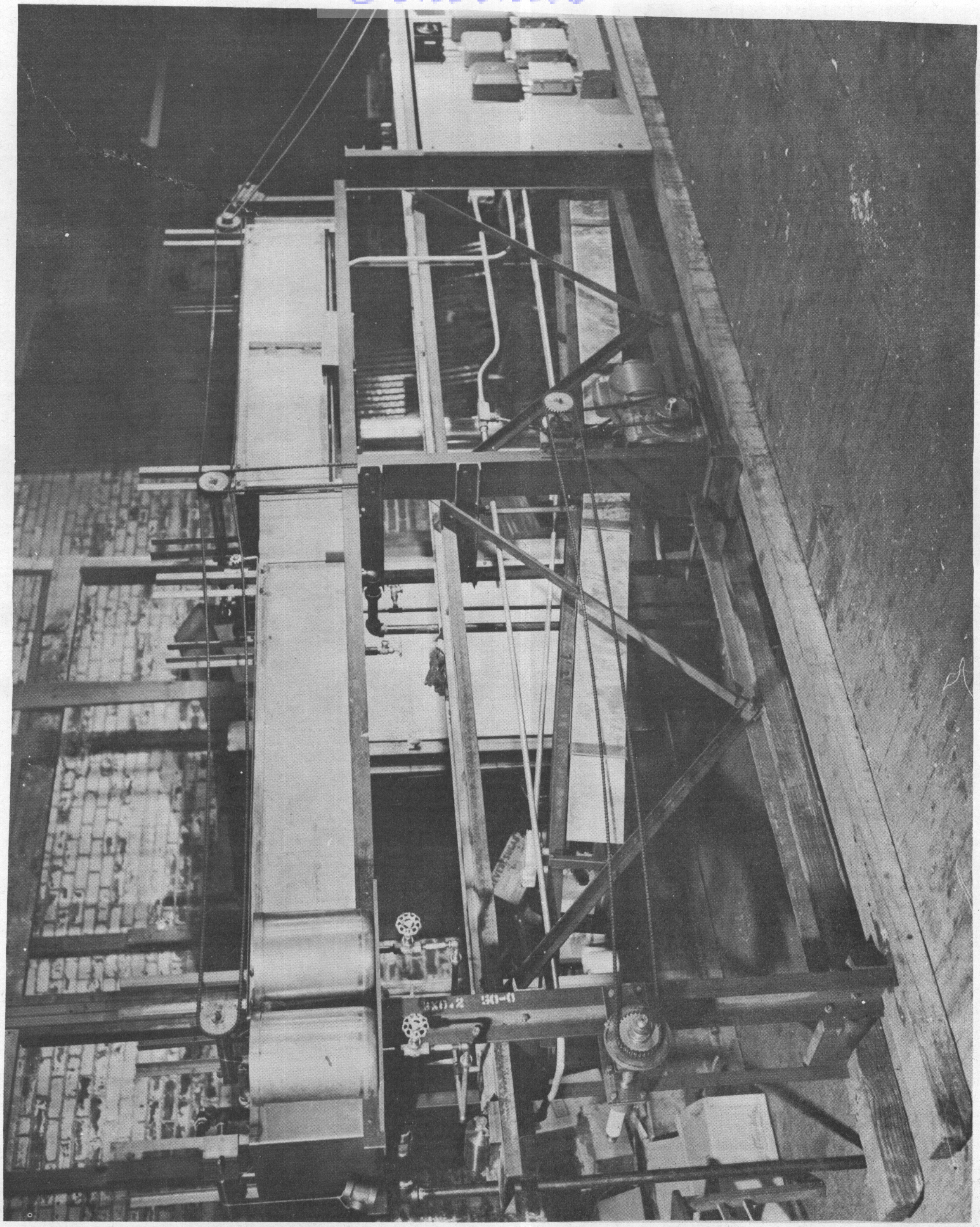



FIGURE 7. CHEMICAL TREATING TANKS

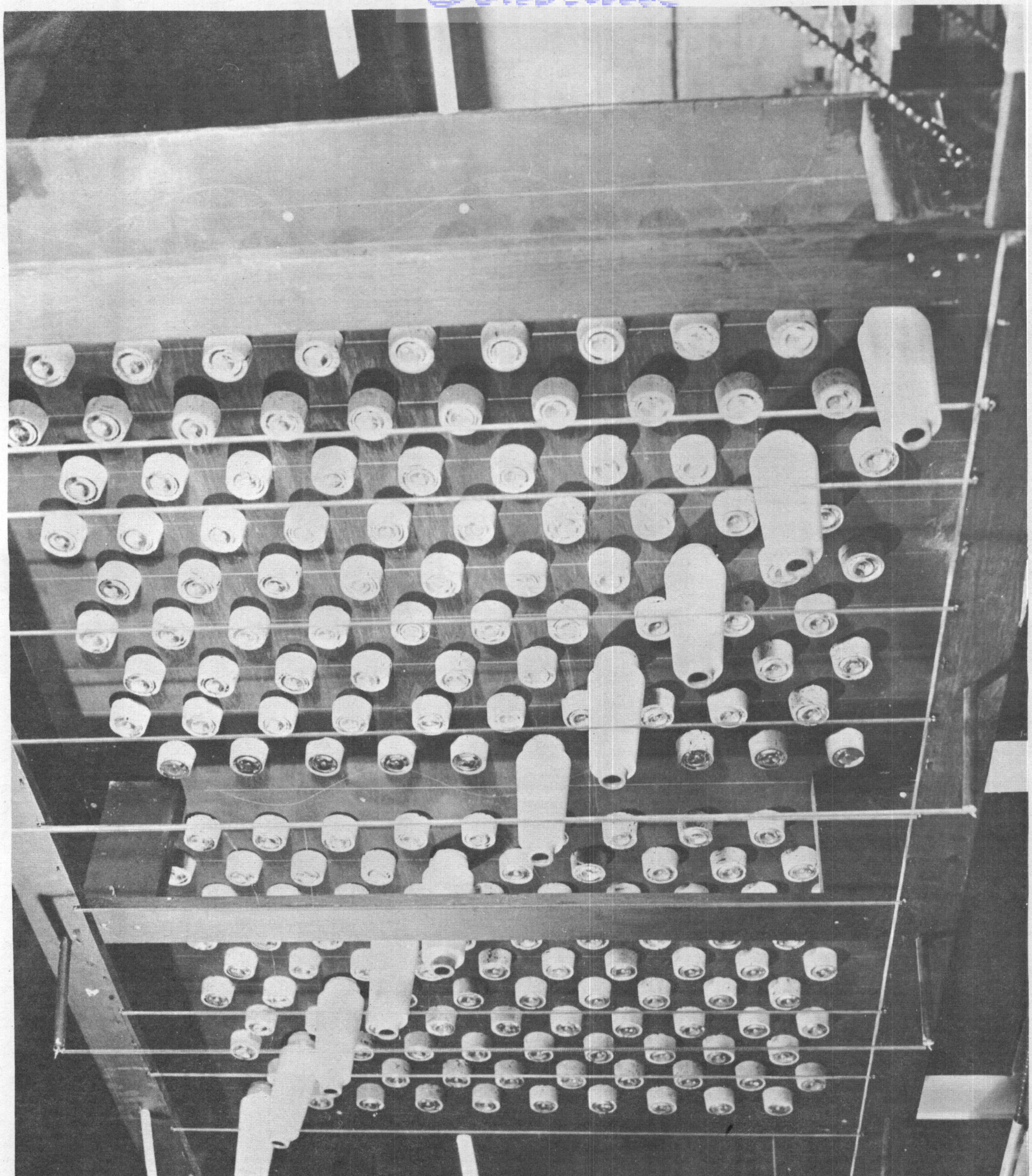


FIGURE 8. FEED ASSEMBLY SHOWING A FEW FEED CONES

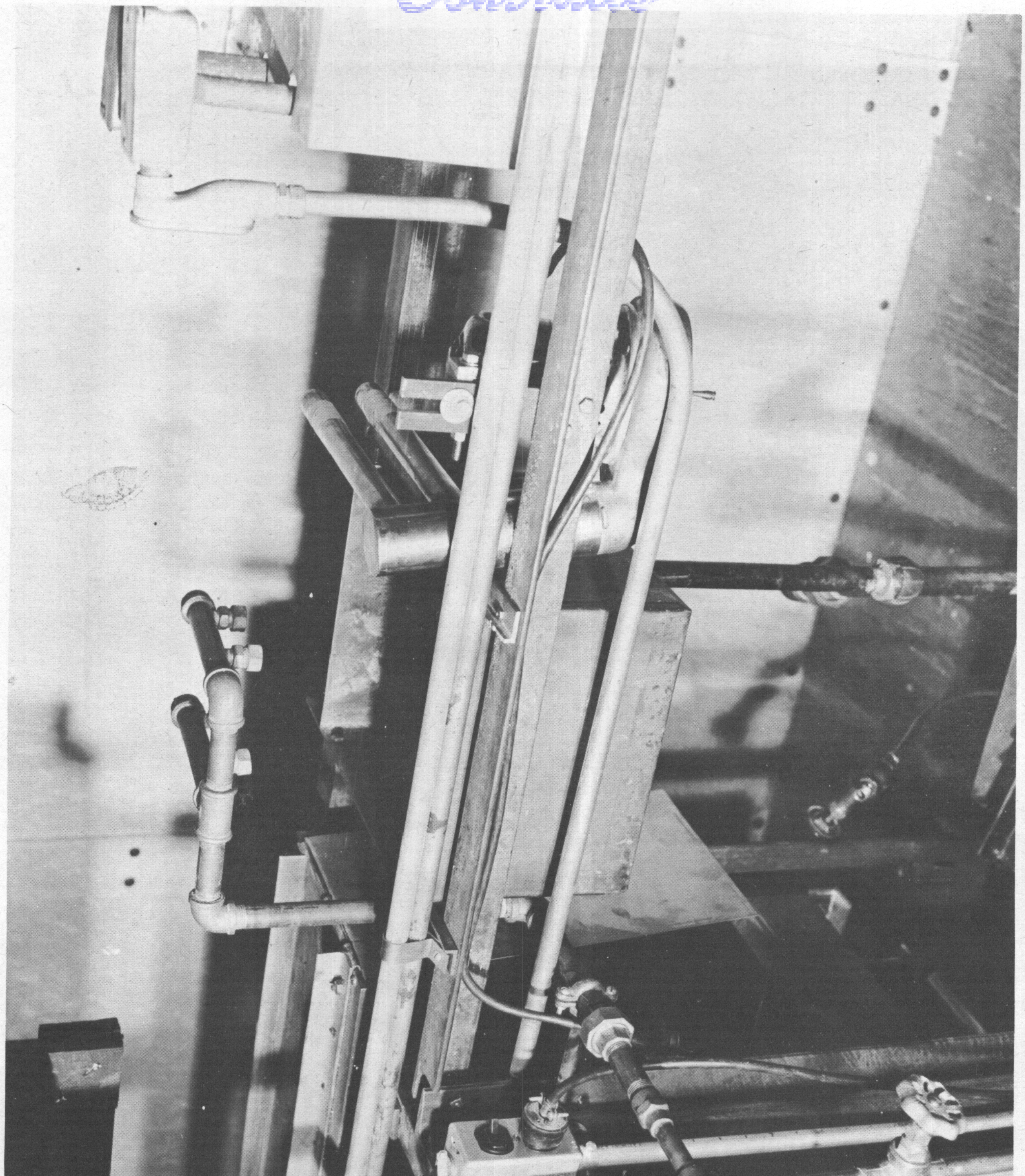


FIGURE 9. SPRAY WASH AND-BLOW DRIER

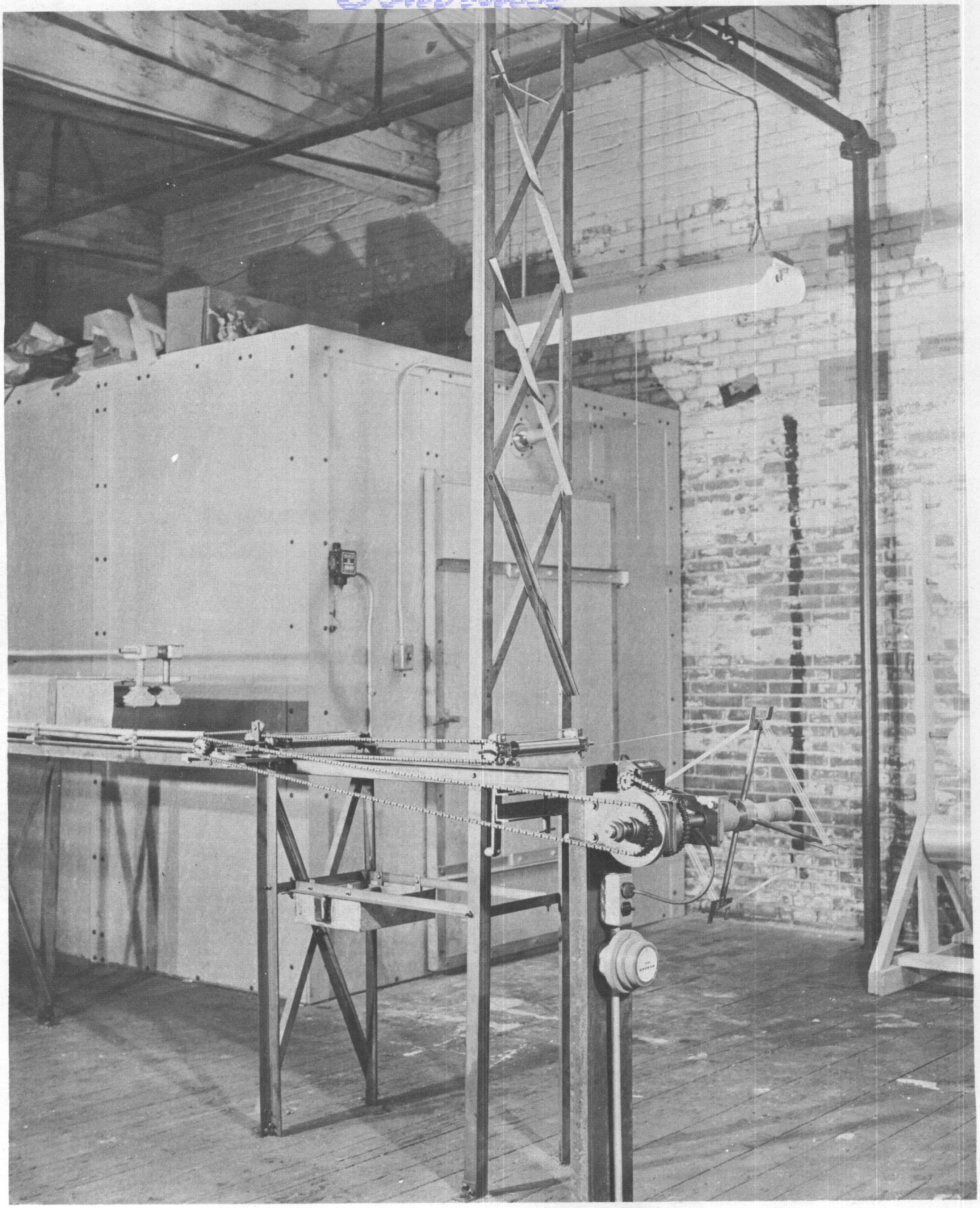


Figure 10. - Lacquer coating tank and windup reel

The chemical deposition method is fundamentally cheap and effective. It is recommended that further work be done with it along the lines of batch silvering nylon hanks and subsequently cutting them to length. This could insure:

1) Maximum silver utilization before recycling.

2) Extremely low labor cost.

3) Very low capital investment with high output capacity.

B. Contract specifications on the product together with comments.

| | Specifications | Comments |
|---|---|---|
| 1. | Monofilament diameter 0.003" ± 0.001" | Product approximately 0.0029" |
| 2. | Metal resistance maximum 100 ohms/in. | Product 10-15 ohms/in. |
| 3. | Good adhesion of coating to monofilament | Adequate |
| 4. | Physically and electrically stable from $-65^{\circ}$ to $+185^{\circ}$F | In general untested. Resistance after 2 months storage at $160^{\circ}$F 10-15 ohms/in. |
| 5. | Packaged so as can be readily cut. | Packaged in 1" x 1-1/2" x 12" cellulose tri-acetate container. Readily sliced. |

C. Various monofilaments.

The following tabulates the result of attempts to procure other monofilaments than nylon:

| Company | Material | Description |
|---|---|---|
| Celanese Corp. of Am. | None | |
| Chemstrand Corp. | Nylon | 10, 15 denier only |
| Am. Viscose Company | None | |
| Owens Corning Fiberglass Corp. | Glass | .0002" to .0004" only |
| E. B. & A. C. Whiting Co. | Polystyrene | .007" up |
| Reeves Bros. Inc. | Polyethylene | .0004" to .0005" |
| Bolta Products | Saran | .005 and .005 x .020 |
| National Plastics Products | Saran | .005 |
| Tennessee Eastman Co. | Cellulose Acetate | No fixed description |

D. Various overcoats

The following tabulates work with various overcoating materials:

| Material | Results |
|---|---|
| 1. MIL Spec. $ZnCrO_4$ lacquer | Flakes badly |
| 2. MIL Spec. Black lacquer, cellulose nitrate base. | Beads |
| 3. Clear cellulose nitrate lacquer | Beads |
| 4. Formvar 5% in ethylene dichloride | Slightly sticky, needs long curing cycle. |
| 5. Nylon in ethyl alcohol: | |
| 20% | Requires doctoring to smooth; makes breaking of fibers frequent. |
| 10% | Beads; sticky |
| 5% | Slightly sticky |
| 2.5% | Good (adopted) |

E. Future machine

1. Cost

The present machine has been operated at 16 feet/min. with 80 fibers in parallel. This represents an output of 1,750,000 feet per day. The variable of speed has never been fully explored. Mechanically, however, present equipment can easily function at three times this rate without change, i.e., at a rate of approximately 5,000,000 feet per day. Since all components of the present equipment are purchasable at a cost of less than $500. it seems indicated that a considerable expansion of throughput can be achieved at quite low cost. Even by the expedient of duplicating equipment, a total cost of $20,000 could result in an installed fiber capacity of in excess of 50,000,000 feet perday.

2. Design

Any future machine, however, could be designed to operate with greater certainty and less attention, provided:

1. The product take-off were semi-automatic
2. The drive were variable in speed
3. The silvering is done as a two or three step operation
4. The nylon is fed direct from full bobbin of two pound capacity.

In light of the batch nature of the fiber input it will probably remain desirable to have any large capacity equipment operated as a number of parallel machines.