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DEPARTMENT OF THE ARMY
QUARTERMASTER RESEARCH AND DEVELOPMENT LABORATORIES
TEXTILE AND LEATHER DIVISION

Textile Dyeing and Finishing Laboratory Report No. 89

ACHIEVEMENT OF LOW INFRA-RED REFLECTANCE CHARACTERISTICS IN NYLON FABRICS WITH REDUCED COPPER SALTS

by

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SUMMARY

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Examination of a sample of nylon shirting material obtained from the DID, through H. A. Delcellier, Lt. Col., Canadian Army, its Director, has revealed IR characteristics which have been achievable heretofore only by subterfuge methods. The results show that this lowering of the IR characteristics may have been fortuitous deriving from the presence within the fiber of a percentage of Cuprous Sulfide.

There is some evidence of probable loose bonding between the copper compound and the nylon based on the fact that the color produced is olive rather than gray, the normal color of Cuprous Sulfide. The durability to laundering is moderate. Fastness to light is that characteristic of the dyes used and does not seem to be influenced by the presence of the cuprous sulfide.

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INTRODUCTION

As in our own case, the Canadian Army is directing its efforts towards the achievement of low infra-red reflectance characteristics in combat clothing for protection against Sniperscope detection. By way of establishing a background based on prior and current deliveries of fabrics, photometric evaluations of materials in storage were made using the U.S.A. Quartermaster Photometer.(1) This survey unearthed a sample of nylon shirting material with unusually good IR characteristics. This was forwarded for our analysis by Col. Delcellier of the Directorate of Inter Service Development, Canadian Army.

The history of this fabric was traced for us. The known facts concerning the processing techniques were submitted for whatever interest they might hold. The salient facts were these:

The IR of the fabric is 24%. The fabric was dyed by the use of Althouse Chemical Company's special nylon dyes: Supernylite Yellow G, Supernylite Brilliant Blue B, and Supernylite Red 7B in the presence of Supernylite Salt which contains Copper Sulfate, Sodium bisulfate and Glauber's Salt. (sodium sulfate) The nature of the water repellant used was indefinite but was either Permel made by American Cyanamid Company or a Silicone, Decetex 104, made by Dow-Corning Company. During the processing flash drying for 1 second at $2100^{\circ}F$ was practiced. Heat setting was accomplished prior to dyeing at $410^{\circ}F$ for 8 seconds.

EXPERIMENTAL AND RESULTS

In view of the stated use of the Althouse Supernylite dyes samples of the three specific dyes were obtained. These were dyed to a match of the Canadian shade. Simultaneously, an examination was made of the various colors in the Supernylite series as contained in a shade-book provided at our request by Althouse Chemical Company. This scrutiny revealed that neither the colors of the shade book or our efforts to reproduce the Canadian shade gave infra-red values even remotely approaching the values noted in the submitted sample. The values of the Supernylite dyes are given in Table I.

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TABLE I

DYE	IR
Supernylite Yellow G	89.1
Supernylite Brilliant Blue B	97.7
Supernylite Red 7B	93.3
Supernylite Yellow NRS	97.7
Supernylite Orange C	93.3
Supernylite Scarlet G	93.3
Supernylite Scarlet B	97.7
Supernylite Maroon LFS	87.1
Supernylite Blue BR	95.5
Supernylite Navy B	93.5
Supernylite Brilliant Green B	97.7
Supernylite Brown 2R	92.5

A study of the effect of Decetex 104 on the infrared reflectance characteristics of nylon dyed with a special chromiferous dye formula showed a reduction in this instance from an initial value of 46% to 40%. In view of the normally higher values of the Supernylite dyes this degree of change was not considered important.

On the suspicion that somehow carbon black might be a factor in the low infrared characteristics noted, the submitted fabric was then subjected to stripping. Spectrophotometric characteristics of the original and of a sample stripped with caustic and hydrosulfite were determined. A sample of the Canadian nylon was then dissolved in formic acid and the solution filtered through a retentive filter paper. The spectral properties of the residue were recorded. These are shown in Fig. #1.

Ash determinations were then made and the constituents qualitatively established by chemical and spectrographic techniques. These revealed the presence of copper and titanium. Since microscopic examination of the dyed nylon showed that it had been delustered, the presence of the titanium was normal; the copper was recognized as originating with the Supernylite salt.

Referring to the recent work accomplished with polyacylonitrile fibers using reduced copper salts, (1) experiments were undertaken with a number of available reducing agents, among them certain sulfur-containing compounds. The acids used were organic acids. Infrared values were still high.

In a further effort to resolve the nature of the low IR agent, samples of the original Canadian fabric were boiled with mineral acids and ammonia. This study showed that the IR values were destroyed by hydrochloric and nitric acids, but not by sulfuric acid even at a pH of 1.5.

TABLE II

EFFECT OF ACIDS AND ALKALIES ON INFRARED
REFLECTANCE OF CANADIAN NYLON

Solution	I. R. R. before	I. R. R. After Boiling
Dilute HCl	20	50
" Nitric Acid	20	58
" Sulfuric Acid	20	21
Ammonium Hydroxide	20	23

With this as basis, the experiments with reduced copper salts were repeated at a pH of 1.5 maximum using sulphuric acid. The best technique proved to be a two-step process.

The cloth was first wetted out at the boil in the reducing compound in the presence of a wetting agent. It was then transferred to a hot acidified solution of copper sulfate, then returned to the reducing bath and finally to the copper sulfate solution again. Subsequently, it was determined that a better technique was to wet the fabric in the copper sulfate solution, then transfer to the hydro-sulfite bath, then again to the copper solution. A color change occurs with a transition from red-brown to olive-green. The infrared properties were excellent. Figure #2 gives the spectral response of the treated nylon as compared to that of the residue from the Canadian nylon.

Fabric was subsequently prepared on the jig. The fabric was padded through boiling acidified copper sulfate solution then through hydrosulfite and finally run 20 ends in the jig with the acidified copper sulfate bath. Similar studies with other reducing agents showed that only sodium thiosulfate behaved in the same manner. No one bath operation seemed possible with the nylon.

Assuming that the end product might be Cupous Sulfide, reference to the literature revealed the following reactions:[3]

With Hydrosulfite

$$Cu + 2Na_2S_2O_4 = Cu + 2SO_2 + 2Na_2SO_4$$

$$6\ Cu + 6H_2SO_4 = Cu_2S + 4CuSO_4 + 6H_2OSO_2$$

With Thiosulfate

$$2\ Cu + 2Na_2S_2O_3 + 2H_2O = Cu_2S + 4H + 2Na_2SO_4 + S$$

A check of deposited sulfur in the nylon treated with the Thiosulfate bath revealed its presence, thus establishing this reaction. Pictures of X-ray diffraction patterns of the original Canadian fabric and of experimentally treated nylon fabrics using the fiber bundle method have demonstrated that the cuprous sulfide is present as the alpha form.

Laundering tests on the original Canadian fabric and on the experimental samples were undertaken using the Atlas Launderometer, at a 30-1 bath ratio and a temperature of 130°F. The detergent was a 1% solution of Nacconol NR; one hundred stainless steel balls were used. The time was 20 minutes. Table III shows these data:

TABLE III

INFRA-RED REFLECTANCE PROPERTIES OF LAUNDERED SAMPLES

SAMPLE	IRR BEFORE LAUNDERING	IRR AFTER LAUNDERING
Canadian	22	32
Jig-Treated Nylon "Hydro-reduction	14	30
Beaker " " " "	12	15
" " " " "	15	17

DISCUSSIONS

The foregoing studies have demonstrated that the effective agent in the Canadian nylon is cuprous sulfide. The only point remaining unexplained concerns the possibility of weak bonding between the copper and the nylon. The normal color for cuprous sulfide is black. The olive color of the treated nylon leads one to suspect the possibility of such bonding. There is likewise the question as to whether copper in complex structure may not exist in the nylon in addition to the cuprous sulfide. Whatever the condition, there seem to be no doubt that at least part of the low infra-red reflectance results from cuprous sulfide since this chemical has been demonstrated to be low infra-red reflecting.

Based on the composition of the Supernylite salt one might reasonably expect that an unusual side reaction had taken place in the dyeing of the Canadian fabric. One such side reaction might result if, in addition to the Supernylite salt, metallic copper were present in a valve or bearing which could be exposed to the acid condition. One further postulate explores the possibility of the dyed fabric having to be stripped because of excessive depth of shade or of uneven effects.

In any event the results are not normal for the Supernylite dyes. The results are not optimum since the stability to laundering is not adequate. However, proper conditions of application leading to greater stability are possible as demonstrated by the beaker dyeings.

CONCLUSIONS

The results herein reported open up a new avenue for the achievement of low infra-red reflectance on nylon. Certain practical problems need solution before commercialization of this process can be effected. Since these studies as reported herein were intended to elucidate the reasons for the unusual characteristics of the Canadian nylon fabric, and since the stabilization of the process for greater laundering resistance constitutes a major program in itself, this report covers only the "detective" work undertaken. That a fundamental new approach to low infra-red properties in nylon has been discovered is only too evident from the data obtained and herein reported. Its extension to other nitrogenous fibers is being explored and promises to be similarly effective.

ACKNOWLEDGEMENT

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Mr. S. D. Bailey of the Pioneer Research Laboratory we acknowledge the assistance of the exray defraction pattern and to Mr. A. Ramsley of the General Testing Laboratory go our thanks for his assistence in obtaining the spectographic data.

LITERATURE:

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2. Feild T.A. and Freman , G.H. Abstracts of papers T.R. 5, Annual Meeting in New York on 16 November 1950.
3. Reference to reactions, Analytical Chemistry, Hall, Treadwell, Volume I. Qualiative, Ninth Addition, John Wiley & Sons.

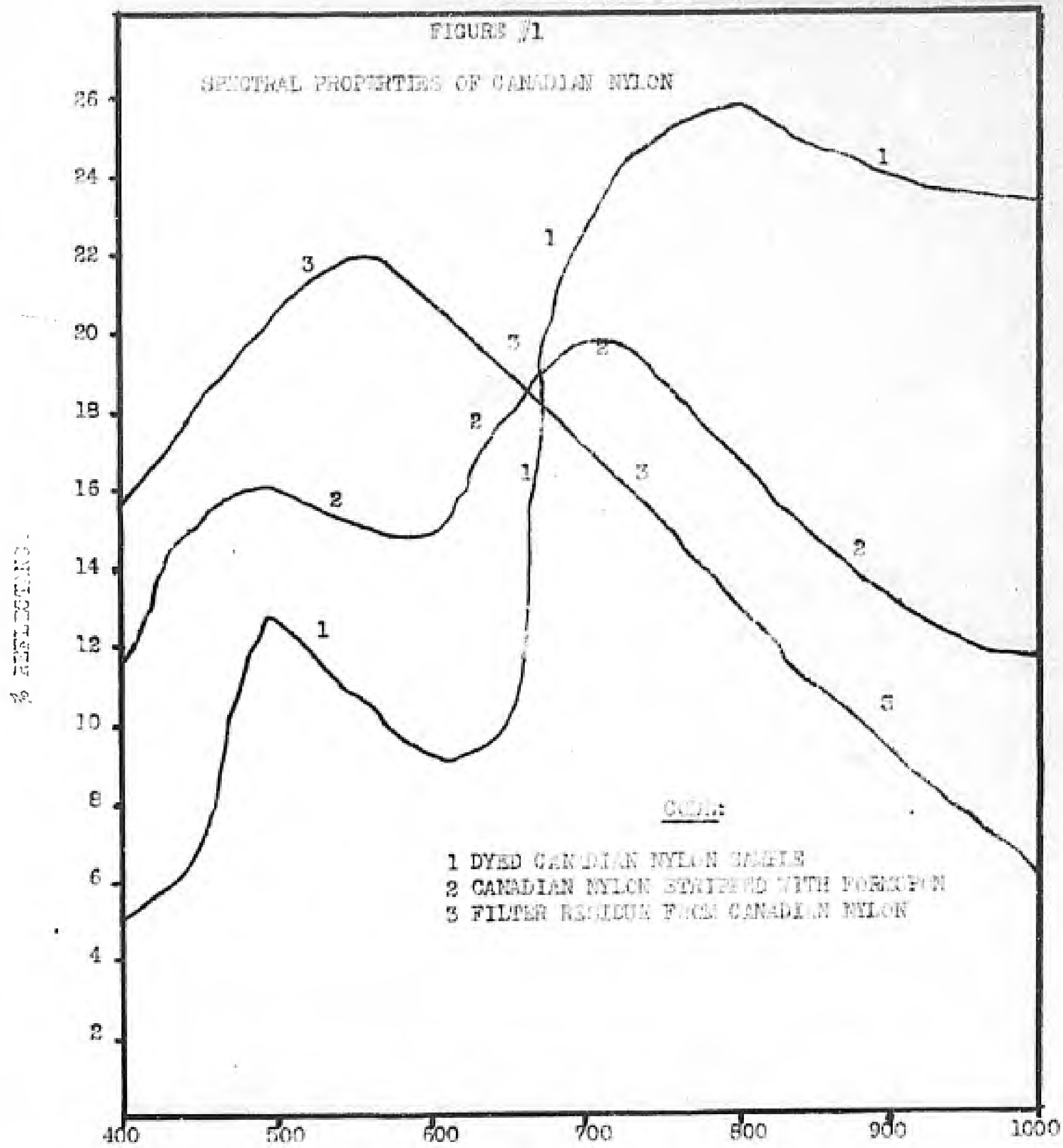

FIGURE #1

SPECTRAL PROPERTIES OF CANADIAN NYLON

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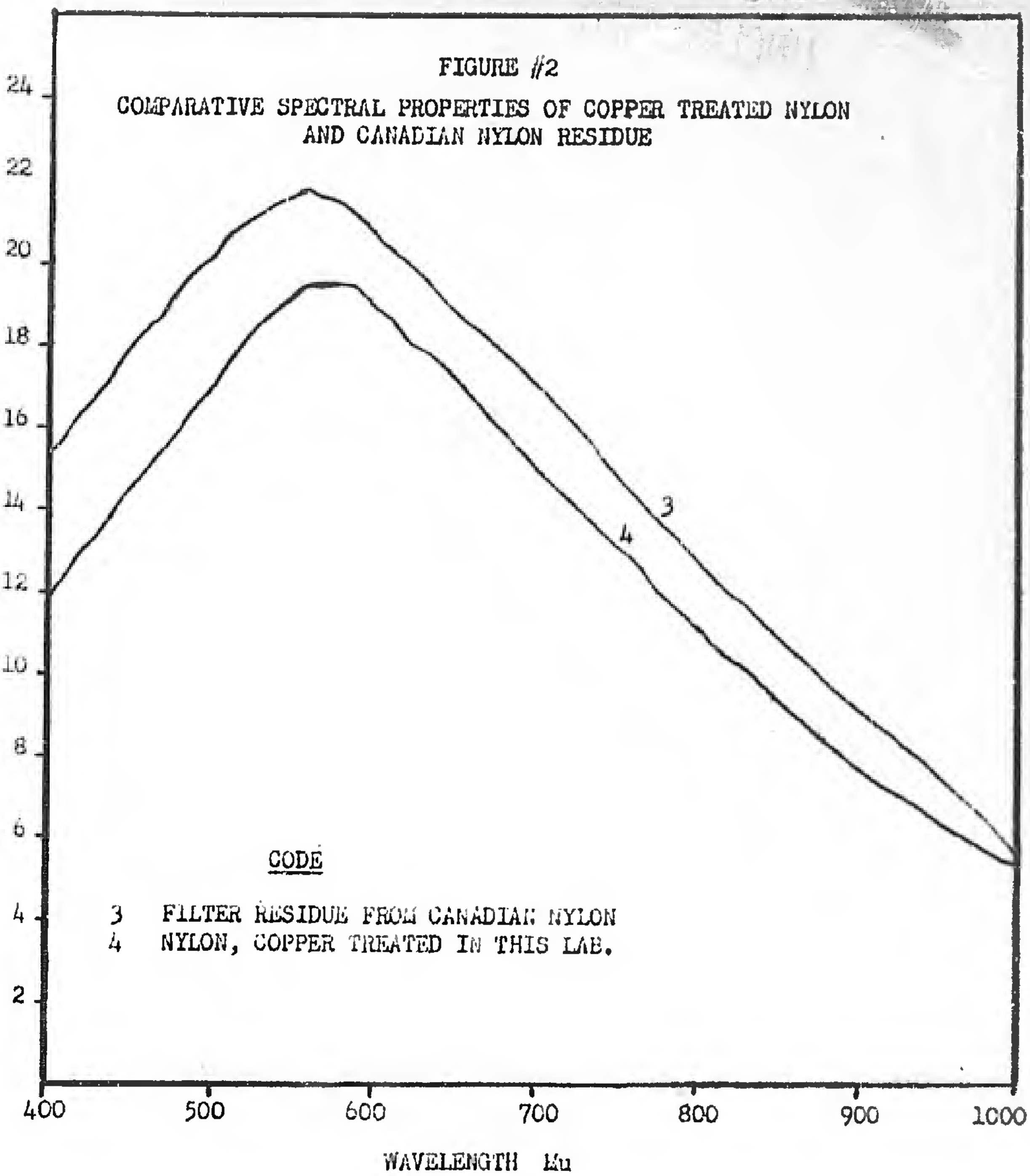
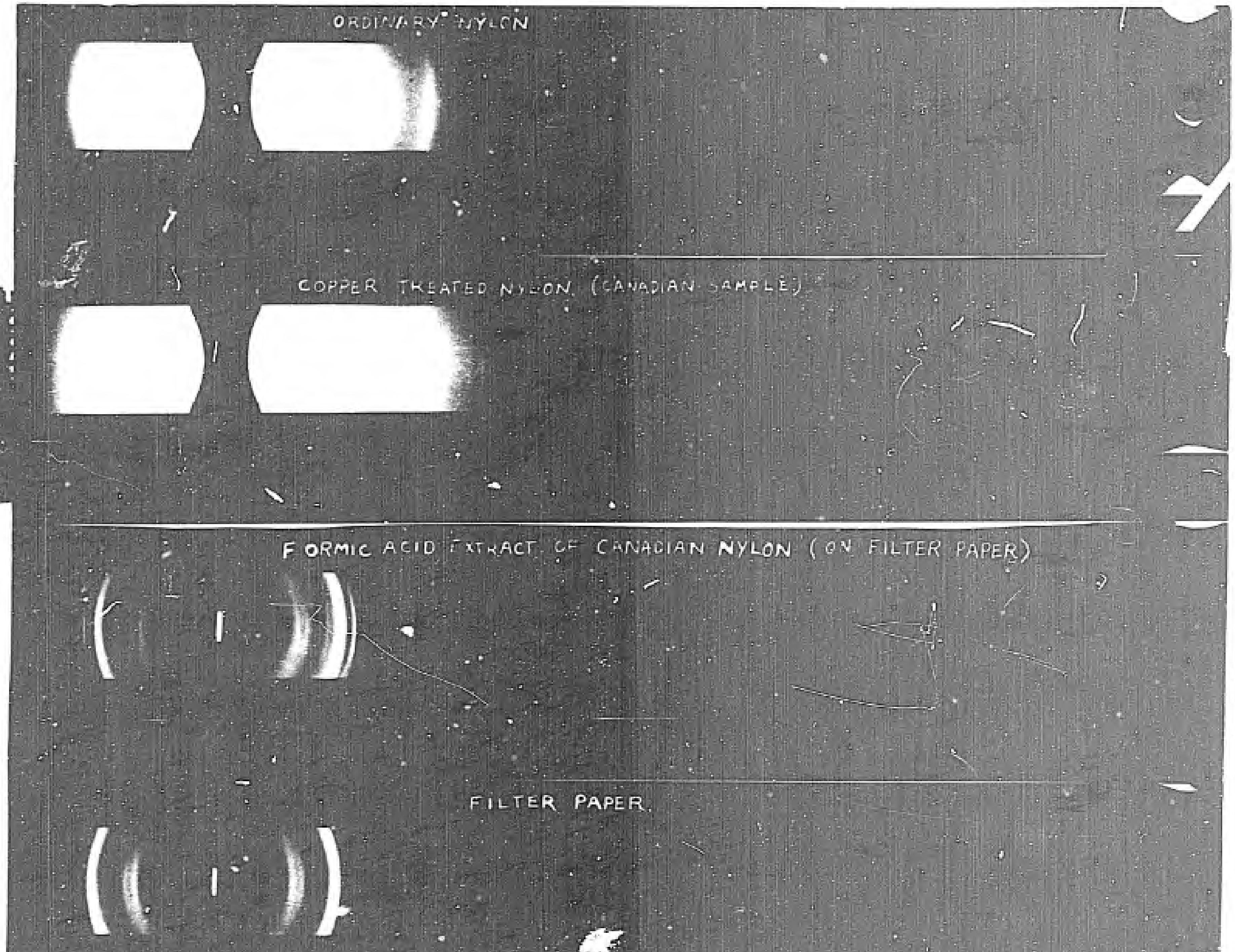
FIGURE #2

COMPARATIVE SPECTRAL PROPERTIES OF COPPER TREATED NYLON AND CANADIAN NYLON RESIDUE




ORDINARY NYLON
COPPER TREATED NYLON (CANADIAN SAMPLE)
FORMIC ACID EXTRACT OF CANADIAN NYLON (ON FILTER PAPER)
FILTER PAPER