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SR, March 6, 1978

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SPECIAL REPORT

PASSIVE DOSIMETERS

by
Michael A. Centanni
and
M. Peter Dreyfuss

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Corporate Research, 4032A-78
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PASSIVE DOSIMETERS

by

Michael A. Centanni
and
M. Peter Dreyfuss

SUMMARY

The Corporate Research New Ventures group has initiated a 1978 Feasibility Study on passive dosimeters. Prior to this, we conducted a preliminary analysis of the technical and business aspects of passive dosimeters as a new business opportunity for BFG. This report summarizes many of our findings.

In their simplest form, passive dosimeters are small badges which can be clipped to the workers shirt pocket. And be used to monitor his personal work environment for air contaminants considered dangerous to his health and safety (ex.: VCM, benzene, lead dust, etc.). The list of chemicals that are monitored in the workplace is large and growing rapidly. Several companies have introduced passive dosimeters based on charcoal absorption. We see no rationale in BFG making charcoal based dosimeters, which are low in technology, and trying to compete in the marketplace. However, we can describe an "ideal" passive dosimeter that would be high in technical content and come much closer to satisfying the needs as perceived by all sides involved (govt., worker, management). Our feasibility study will be directed towards this "ideal" dosimeter and we discuss some technical concepts that might lead us to our goal.

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CONCLUSIONS

1. The number of chemicals that are considered harmful to workers are large and growing in number daily. Many are already being regulated in terms of worker exposure. Monitoring the work environment for these chemicals will represent a significant and growing market for selected companies.. We do not know if BFG should or will be one of those companies but we feel a need to make sure the opportunity doesn't go by unnoticed.

2. BFG should not attempt to market a carbon absorption dosimeter because of the low technology involved and lack of a proprietary position.

3. If BFG is to compete, it should develop passive dosimeters that essentially eliminate the expensive chemical analysis step.

4. An "ideal" passive dosimter has the following features

   - good (less than 1 ppm) sensitivity
   - good selectivity
   - instant (plug-in) analysis
   - small size and light weight
   - represent a net cost savings to the user
   - be capable of recording peak exposures

RECOMMENDATIONS

The authors have initiated a feasibility study (4032A) and along with Sudhir Shringarpurey of Avon Lake Technical Center and Dan Hine, are currently working on the project.

OBJECTIVES

To consider and evaluate the business and technical opportunities in the area of passive personal chemical monitors.

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PATENT SITUATION

Patents exist covering certain aspects of current badges. However, the new high technology badges that we propose to develop should allow for adequate patent coverage of our discoveries and developments.

All passive dosimeters of the type here considered will probably require a static airgap. At least some aspects of this are disclosed and claimed in U.S. 3,950,980 assigned to the 3M Company (April 20, 1976). The claims seem rather narrow. Nevertheless, it seems there might be some litigation between 3M and Abcor (Walden Div.) on the basis of this patent. We do not know if there is or not. In any case, the Patent Law Department will have to carefully consider and render a judgment on this point.

ACKNOWLEDGEMENTS

Two "idea generation" meetings were held by D. Dickens and P. Zakriski in early 1977 as a means of identifying those people in the Company who might contribute to this project. We want to thank those involved, W. Kroenke, A. Berens, R. Whitehead, C. Carman, P. Nicholas, R. Childers, F. Doljack, A. Magistro, F. Ramp, R. Hooser, and Lee Traynor, for their time and subsequent discussions. In addition, we want to acknowledge conversations and significant help from Ron Myers, Sudhir Shringarpurey (ALTC), and John Born.

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INTRODUCTION

A well-known problem of increasing concern to BFG is industrial and chemical pollutants and government regulation thereof. The need to control and monitor these pollutants is commanding an ever-increasing amount of effort and expense. Can we turn this situation around to the extent that we can use it to generate business opportunities? One way to do this might be to develop and market new, novel, and effective monitoring devices. Such a business could involve selling only the devices; it might include a newly developed specialty instrument to read the results obtained by the device; or it might include a service wherein we analyze and report the results, offering us the opportunity to establish a service related business. We were asked by means of this report to discuss and record the considerations we explored in the area of personal passive dosimeters as a new business opportunity. These considerations were preliminary to our undertaking a project in developing just such a new product.

Some of the devices already in existence, which we have considered are: the Bendix Pump Monitor and the pumpless carbon absorption badges including a static air gap badge and a membrane diffusion badge. Some newer developments include 3 M's mercury badge; a modification of this concept by Scheide and Taylor[1] who used a quartz crystal as a micro-balance for determining exposure to mercury; and finally, a badge developed by Sudhir Shringarpurey[2] at the Avon Lake Technical Center for detection of organo-tins.

We shall present some background information on all of these devices in the following paragraphs. We feel that it is necessary to inform ourselves and other interested people of these existing devices so that our directives can be more clearly defined.

In the following paragraphs, we shall discuss both dynamic dosimeter and passive dosimeters which are already available on the market. We shall also discuss several new approaches to passive dosimeters.

<u>A. Bendix Pump Monitor</u> -- The Bendix Pump Monitor has been in use at BFGoodrich since 1974. In that year we were faced with the urgent problem of how to effectively monitor employee's exposure to vinyl chloride monomer (VCM). The Bendix Pump Monitor has filled that urgent need since then. Over the years, we have gained much experience in the operation of the pump.

These first generation badges use a mechanical pump to cycle air at a fixed rate through a tube containing activated carbon. At the end of the day, the tube is sent to the lab where it is analyzed for VCM. This analysis is both time consuming and costly.

In addition to the expense of analyzing the tubes, there are other disadvantages to the pump monitor. One of the biggest

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disadvantages is their expense. Initially, they are about $300 a piece. They can be used many times over; however, the expense associated with maintenance can be very large. They are mechanical devices that are prone to breakdown. This brings us to an interesting point; if the pump breaks down when an employee is wearing it, will the employee report it so that the malfunction can be corrected? If not, then the reliability of the pump drops to nearly zero. In addition to being expensive and possibly unreliable, the pumps are noisy, bulky, and uncomfortable.

B. Pumpless Carbon Absorption Badges -- Since we are calling the Bendix Pump Monitors the first generation devices, these devices will be termed second generation devices. These badges are in the market development phase of commercialization by several companies and are under current evaluation by BFG. In fact, they will very likely replace the pump monitors. They are the badges of the immediate future.

1. Static Air Gap Badge -- There are presently two suppliers of the static air gap badge. They are Abcor[3] and 3M[4,5] These badges also use activated carbon but instead of a pump, they employ a static air gap across which the pollutants diffuse to the carbon absorbent.

Both badges use a draft shield made from a non-reactive porous material to isolate the air gap. The 3M badge uses a thin microporous film of isotactic poly(propylene) for such a shield. These wind screens insure that the amount of gas available to react with the activated carbon is a function of concentration. In both cases, the amount of gas collected is quite independent of the velocity and impingement angle of the gas mixture. Furthermore, both badges yield a time-weighted-average for exposure to solvent mixtures with the Abcor badge yielding information in the 0.5 - 150 ppm range.

There are several apparent advantages of these second generation badges over the first generation badges. For example, the badges are passive devices and therefore require no maintenance. They are light-weight, simple, and seem to work. Furthermore, their cost is very low. In fact, the Abcor badges come to $3.72 per badge; on the other hand, the pumps, according to Abcor, come to either $4.80 or $6.80 a piece depending on whether you already have the pumps or whether you have to buy them. See Table 1 for the breakdown on pricing.

One of the disadvantages of these carbon absorption badges is that they are still carbon absorption devices. In this area, the technology has been somewhat stagnant. Of course, the analysis is the same as the pump analysis. Again, these analyses are both time consuming and costly.

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TABLE 1[6]

Abcor's Cost Comparison Table

	Customer A has 5 Air Sampling Pumps	Customer B Must Purchase 5 Air Sampling Pumps	Custon r Sampling witl Gas Badge Org nic Vapor D simeter
Initial Outlay	-----	$1,500 5 pumps @ $300.00	95.00 5 Dosin ters @ $19.00
Usual Life	?	3 years	1 year (50 uses)
Maintenance	$50/pump	$50/pump	ONE
Depreciation	-----	5 @ $100/year	5 $19.00
Usage	1 day/week	1 day/week	1 ay/week
Cost Per Use			
Depreciation	-----	$2.00	$ .37
Maintenance	1.00	1.00	---
Charcoal Tubes/ Replacement Elements	0.80	0.80	.95
Supervision Time, Set Up and Calibration Labor @ $6.00/hour	3.00	3.00	.00
Cost Per Sample Collected	4.80	6.80	.32
Less Interest on Capital Not Tied Up in Air Sampling Pumps @ 10% on Pretax Basis	----	----	.60
Net Cost Per Sample	$4.80	$6.80	$ .72

2. Membrane Diffusion Badge -- This badge, marketed by Real, uses a silicon rubber membrane as a diffusion membrane. Since it is a diffusion controlled device, we feel that the response time of the badge may be too slow, making it ineffective and unsuitable. Furthermore, their prices are very high, nearly \$40 per badge, excluding analysis.

C. New Developments -- We shall call these badges third generation badges. These badges move away from carbon absorption and work toward chemical fixation and new absorption techniques. There are presently two examples of such badges.

1. The first example is 3M's mercury vapor badge. It's cost is \$20 including analysis and reporting of the results. Analysis appears to be simple and inexpensive. The badge consists of a thin film of gold on a substrate. The mercury forms an amalgam with the gold and hence changes the conductivity of the gold. Therefore, in this case, the analysis is a simple conductivity measurement.

2. The second example is given by the work done by Scheide and Taylor at the National Bureau of Standards[1]. In their work, they used a quartz crystal as a sensitive micro-balance. The concept is to monitor the resonant frequency of a quartz crystal which is part of an active circuit. Interaction with the pollutant is accomplished through a chemical which is coated to the surface of the quartz. A gain or loss in weight will alter the resonant frequency of the system (quartz plus coating). Scheide and Taylor have used this idea as a monitoring device for mercury vapor. They used gold as a fixant and were able to obtain a sensitivity of fractions of a part per billion in concentrations of mercury. An attractive feature of these sensors is that they are reversible. The mercury can be removed by heating the crystal in an oven at 150°C in a stream of clean dry air.

Scheide and Taylor were also able to show that air passed over the sensor at rates up to 300 cc/min does not affect the sensor stability. Minute changes in frequency occur when the flow is started and stopped. They attribute this fact to the adsorption and desorption of moisture from the substrated. Since all the crystals used were AT cut (a cut made at 35° 18' to the Z axis), small variations in room temperature did not affect their stability in frequency. In addition, they determined that at flow rates of 100 cc/min, the response of the crystal was constant. The response was linear at higher flow rates but the sensitivity decreased and therefore, the precision of the measurements decreased. The range of the detector was 500 nm (ΔF = 50 hertz). Their work dealt only with prototypes, no efforts to put into the form of an area or a personal monitor were reported.

We are presently considering this means of using a quartz crystal for a badge to detect organic pollutants. The problem becomes finding a chemical which will fix the particular pollutants under consideration. In this particular type of detection system, interferences can be a big problem. In fact, any molecule which sticks to the substrate can change the resonant frequency of the quartz chip and therefore, give false readings.

3. The third example is given by an organo-tin badge developed at BFG by Sudhir Shringarpurey at the Avon Lake Technical Center. This particular badge, in its current stage of development, uses chemical fixation, but in combination with a mechanical pump. Since this badge uses a pump, it's not quite a third generation badge but lies somewhere in between a second and third generation badge.

NATURE OF THE BUSINESS OPPORTUNITY

A. Potential Market Size -- With the advent of the following government associations: N.I.O.S.H. (National Institute for Occupational Safety and Health), E.P.A. (Environmental Protection Agency), O.S.H.A. (Occupational Safety and Health Administration), and T.O.S.C.A. (Toxic Substances Control Act), stringent regulations on occupational exposure to dangerous chemicals have been forced upon industry. These regulations have nearly insured a large and growing market for personal monitoring badges. Limits have been set for both a peak exposure and for a time-weighted-average exposure. The latter was based on a 10-hour workday, 40-hour workweek. Let us examine benzene, for example. The occupational exposure of benzene should not exceed one part per million for a 10-hour workday, 40-hour workweek. N.I.O.S.H. estimates that over two million people in the work force are exposed to benzene. Table 2 lists, in addition to benzene, other dangerous chemicals along with their time-weighted-average exposures and the estimated number of people in the work force exposed to the chemicals.

Of course, the pollution does not stop at the workers. For instance, N.I.O.S.H. estimates that in large industrial cities, atmospheric concentrations of inorganic mercury approach a level of one microgram per cubic meter. The number of people exposed to sulfur and nitrous oxides is so large that N.I.O.S.H. will not even hazard a guess as to the number of people exposed. Just consider, for example, the number of policemen and firemen exposed daily to such pollution.

B. Possible Approaches -- There are several ways in which we could move into the market. To begin with, we could sell a new and unique badge in addition to giving technical assistance. Another possibility is to sell a new badge and offer an analytical service either internally or contracted externally to BFG. Furthermore, we could sell a new and novel data analysis instrument. We could use our technology and develop a new and unique area monitor. Finally, we could just license and/or sell our newly developed technology.

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TABLE II

	N.I.O.S.H. estimated number of workers exposed to the chemical	Time-Weighted-Average Exposure for a 10-hour Workday, 40-hour work-week unless otherwise specified
1. Benzene	2,000,000	1 ppm (32 mg/m^3)
2. Inorganic Arsenic	1,500,000	2 μg/m^3 (15 minute sampling period)
3. Ammonia	500,000	50 ppm (5 minute sampling period)
4. Trichloroethylene	200,000	100 ppm
5. Methyl Alcohol	175,000	200 ppm
6. Inorganic Mercury	150,000	0.05 mg/m^3
7. Vinyl Chloride Monomer	---	1 ppm

C. Competition --

1. Commercial -- There are already several second generation badges and at least one third generation badge on the market. They are produced by Abcor and 3M. Both companies make a passive carbon absorption badge. In addition, 3M makes a mercury vapor badge which is definitely third generation. It is highly probable that more will appear on the market. In fact, 3M has been working in this area for several years. Moreover, they have a division of occupational health and safety products. The company is both innovative and aggressive and will certainly develop more monitors.

2. Government -- N.I.O.S.H. is a government sponsored research agency that is currently interested in personal monitoring devices. In their case, however, the projects are generally specific and not very likely to result in a competitive product. Apparently, the National Bureau of Standards is also interested in such monitors as exhibited by the work done by Scheide and Taylor.

3. Universities and Research Groups -- Many universities and research centers are involved in badge studies. One research group currently involved is the Gulf South Research Institute. They do contract work for both the government and for industry. Paul Zakrisky has interacted with them and inquiries about GSRI should be directed to him.

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Both Louisiana State University and the University of Toronto have done extensive work on personal monitoring devices. These are just two universities of many that are involved in such work.

The University of Toronto has recently published a paper on the monitoring of nitric oxide.(7) The nitric oxide forms a second stable radical with the free radical reagent, 2-phenyl-4,4,5,5-tetramethylimidazoline 3-oxide 1-oxyl. The free radical reagent is applied in chloroform solution to silica gel plates. The second radical, formed after the reaction, is quantified by electron spin resonance. It is certainly feasible that such work may lead to patent and licensing rights.

NATURE OF OUR TECHNICAL STRATEGY

In our approach, we hope to learn from chlorinated substances and Shringarpurey's organo-tin badge. We are certainly technically competent in chlorinated materials, and are already well into high technology badges with the organo-tin badge.

In our opinion, the largest markets are represented by benzene, acrylonitrile, sulfur and nitrous oxides, carbon monoxide, asbestos, and heavy metals such as lead, mercury, beryllium, and arsenic. We will concentrate our efforts in some of these materials as the project develops.

A. The Ideal Badge -- We have considered the desirable characteristics of an ideal badge. During our work, we will keep these attributes in mind. To begin with, we need a badge that is sensitive; the threshold limit values of many dangerous chemicals are on the decrease. Certainly, a badge sensitive to one part per billion is more than adequate. The badge should provide for easy and fast read-out of the pollutant concentration. Another attractive feature would be to have available the read-out of both the time-weighted-average and the peak exposures. We would like the response to be in direct proportion to the pollutant concentration inhaled by the wearer. Interferences should be kept to a minimum. Finally, where more than one pollutant is present, synergistic effects should be taken into account by the badge. The following table summarizes these characteristics.

One must keep in mind that the real product will inevitably be a compromise but the more we can incorporate into the badge, the better chance we have of developing a highly marketable product.

TABLE 3

Characteristics of an Ideal Badge

1) Sensitive to one part per billion.

2) Should provide for easy and fast read-out of pollutant concentration.

3) Read-out both time-weighted-averages and peak exposures.

4) Badge response in proportion to the pollutant concentration inhaled by the user.

5) No chemical interferences.

6) Synergisms taken into account.

7) A new economic savings over existing methods.

B. Chemical and Physical Fixation --

1. Chemical -- Under chemical fixation, there are several concepts that we are considering. They are:

1) covalently bond a specific chemical reagent for a given pollutant to a polymer matrix.

2) absorb these specific chemical reagents on a substrate; for example, silica or a poly crown ether.

3) use of strong oxidants such as potassium permanganate.

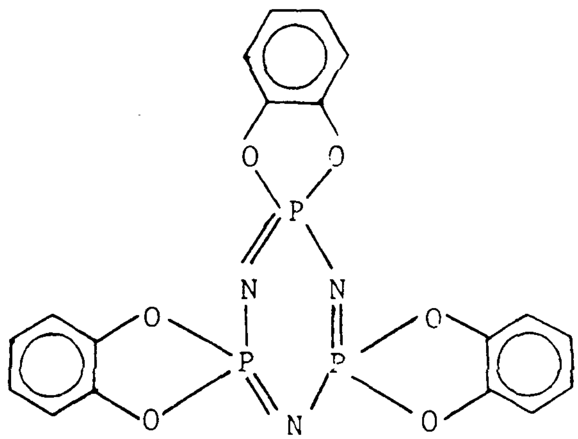
4) use of inorganic olefin complexes.

5) badges which change color such as $PdCl_2$ when exposed to CO.

6) badges which use electrochemical cells.

2. Physical -- Recently, Ron Myers has brought to our attention one of a class of clathrate substrates.[8] The one we looked at is Tris(o-phenylenedioxy) cyclotriphosphazene, which upon contact with an organic compound undergoes a structural change from monoclinic or triclinic to hexagonal with consequent inclusion of the organic compound into the crystal lattice. The molecular weight of this material is 459 and it requires two host molecules

to retain one guest molecule. Its melting point is 244°C - 245°C and it has the following structure:



On the one guest to two host molecules premise, we have calculated a gain in weight of about 10% for toluene as the guest substance. Experimentally, under saturation conditions, we obtained weight gains in the range of 9% to 10% for all three samples of varying sizes. It must be emphasized that these results are very preliminary.

C. New Analytical Methods -- As previously mentioned, one idea we have, which incorporates a new analytical method, is the use of a quartz crystal as a sensitive micro-balance. This would lend itself to direct and fast read-outs. We may consider using a micro-processor as an analyzing unit. At this time, selling both the badge and the instrument looks attractive.

D. Potential Problems -- We cannot anticipate all the problems that can occur in this effort. However, besides the more obvious problems related to not achieving the "ideal" badge performance, we have uncovered some other problems that warrant attention:

1) field testing - will outside firms test our badge and share their data with us?

2) certification - how do we do about getting our badge certified by N.I.O.S.H.?

3) regulated nature of market - the government really controls the rate of market expansion by introducing new chemicals on their list of toxic substances and by altering the limits of exposure of the same.

4) other means of solution - some businesses may shrink. For example, the removal of enough VCM from the resin so that the residual amount is below the threshold limit value would reduce the market for a VCM passive dosimeter.

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5) peak exposure - how important is it to be able to detect peak exposures? Will the government make the monitoring of peak exposures a regulation?

E. Internal Use of Our Technical Results -- We feel that BFG is interested internally in the use of passive dosimeters to monitor personal exposure to dangerous chemicals. Of course, our immediate interest is with the detection of VCM. As a result of this, our main thrust will be in this area. If we do develop such a badge, the capability of in-house testing will aid us tremendously in evaluating the effectiveness of the badge.

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