Research Need 1: Characterize exposure among workers

Robert F. Herrick Sc.D., CIH

Harvard School of Public Health

From: Twenty-seventh Report

Novel Materials in the Environment: The case of nanotechnology

ROYAL COMMISSION ON ENVIRONMENTAL POLLUTION

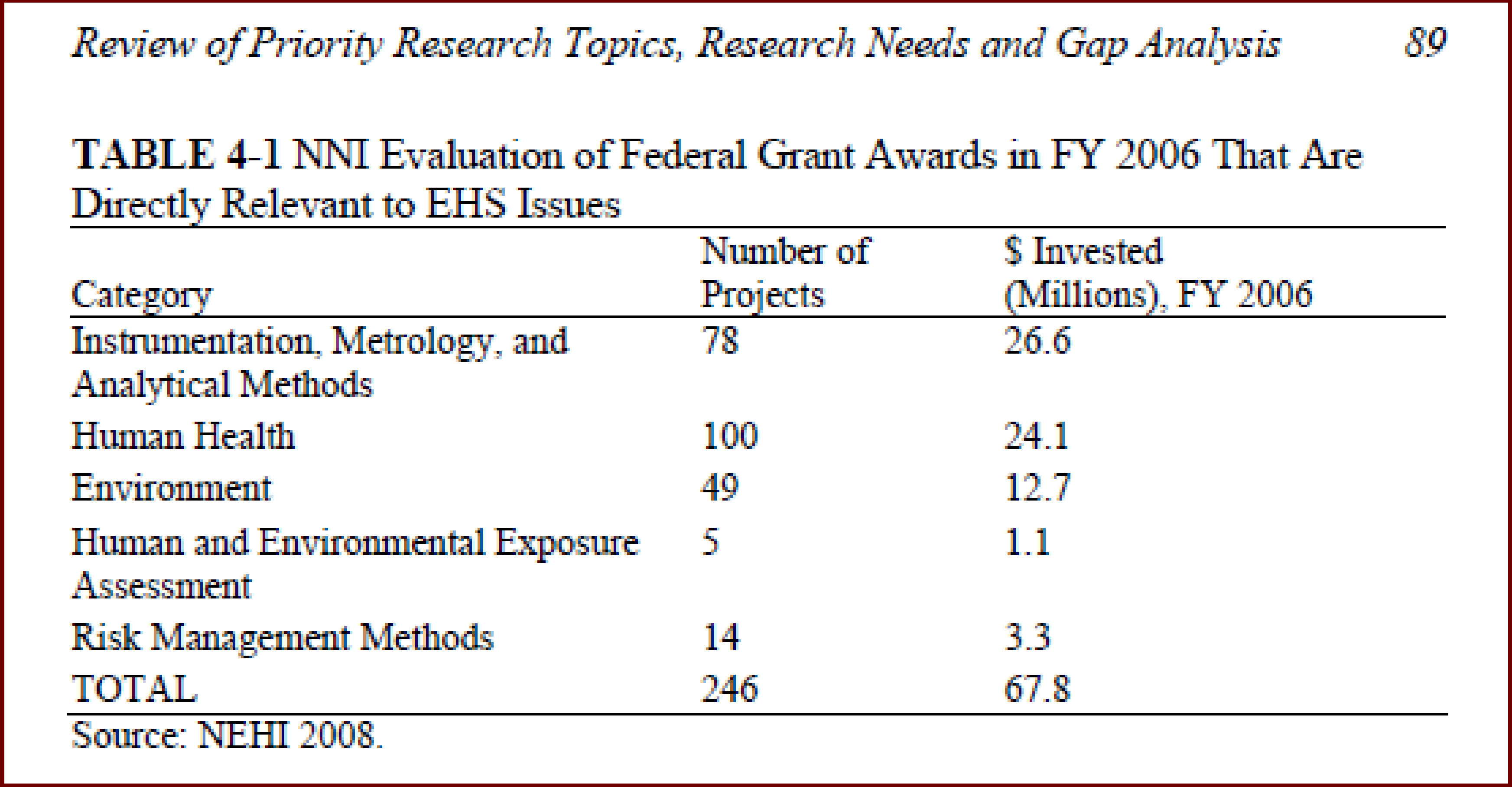
CHAIRMAN: SIR JOHN LAWTON CBE, FRS

…there have been long-standing uses of what we now recognise as nanomaterials, as illustrated by the Lycurgus cup….The Lycurgus cup is thought to have been made in Rome in the 4th century AD. The cup is the only complete example of a very special type of glass, known as dichroic, which changes colour when held up to the light. The opaque green cup turns to a glowing translucent red when light is shone through it. The glass contains tiny amounts of colloidal gold and silver, which give it these unusual optical properties.

Two broad topics

- *Develop qualitative and quantitative exposure survey protocols*
- *Explore utility and feasibility of exposure registries*

Where does human exposure assessment stand?



Review of Priority Research Topics, Research Needs and Gap Analysis *89*

TABLE 4-1 NNI Evaluation of Federal Grant Awards in FY 2006 That Are Directly Relevant to EHS Issues

Category	Number of Projects	$ Invested (Millions), FY 2006
Instrumentation, Metrology, and Analytical Methods	78	26.6
Human Health	100	24.1
Environment	49	12.7
Human and Environmental Exposure Assessment	5	1.1
Risk Management Methods	14	3.3
TOTAL	246	67.8

Source: NEHI 2008.

Where does human exposure assessment stand?

Search term	Medline Citations	ISI Web of Science Citations
nanoparticles	20416	75479
nanoparticles analysis	5208	9748
nanoparticles measurement	514	1951
nanoparticles exposure	21	1246

Develop qualitative and quantitative exposure survey protocols

- How can potentially exposed groups of workers be systematically identified?
- Can existing public health geographical information systems (GIS) and infrastructure to be used for effective sharing of nanotechnology occupational safety and health data including exposure data?
- Can personal exposures be measured?
- Are there adequate emission measurement protocols? What are the limitations?
- How can emission measurements be translated to personal exposures?

Explore utility and feasibility of exposure registries

- *Are exposure registries feasible?*
- *What are the limitations?*

Develop qualitative and quantitative exposure survey protocols

- How can potentially exposed groups of workers be systematically identified?
  - This can be approached from 2 directions, both of which are founded upon existing interagency capabilities
  - First is to link with the EPA Nanoscale Materials Stewardship Program

As described in the EPA "**Concept Paper for the Nanoscale Materials Stewardship Program under TSCA",** the program goals are to:

- Help the Agency assemble existing data and information from manufacturers and processors of existing chemical nanoscale materials;
- Identify and encourage use of risk management practices in developing and commercializing nanoscale materials; and
- Encourage the development of test data needed to provide a firmer scientific foundation for future work and regulatory/policy decisions.

From the NMSP Reporting Form

Occupational Exposure –Please provide the description of worker activity, physical form of the chemical substance, number of workers exposed, and duration of activity. Researchers should only describe unique activities and not standard laboratory practices. Make separate confidentiality claims by marking (X) the “Confidential” box next to any item you claim as confidential.

- (1) -- Describe the activities (i.e. bag dumping, tote filling, unloading drums, sampling, cleaning, etc.) in which workers may be exposed to the substance.
- (3) -- Describe any protective equipment and engineering controls used to protect workers.
- (4) -- Indicate the physical form(s) of the chemical substance (e.g., solid: crystal, granule, powder, or dust) and % chemical substance (if part of a mixture) at the time of exposure.
- (6) -- Estimate the maximum number of workers involved in each activity for all sites combined.
- (8) and (9) -- Estimate the maximum duration of the activity for any worker in hours per day and days per year

From the NMSP Reporting Form

Worker activity (i.e., bag dumping, filling drums) (1)	CBI (2)	Protective Equipment/ Engineering Controls (3)	[redacted]	Physical forms(s) and % substance (4)	[redacted]	CBI (5)	# of Workers Exposed (6)	CBI (7)	Maximum	duration	CBI (10)
									Hrs/day (8)	Days/yr (9)	

Job title(s) of workers exposed

Companion activity

- Conduct a national survey of potential occupational exposures in nanotechnology
- Follow the model of the NOES (National Occupational Exposure Survey, http://www.cdc.gov/niosh/docs/2002-126/2002-126.pdf)

- Design the survey to describe and characterize potential exposures associated with the unit processes throughout the life cycle, including nanomaterial R&D, manufacturing, downstream applicatons incorporating nanos into other products, destruction and disposal, including process wastes

National Nanomaterial Exposure Survey

- Do this first as an inventory, primarily qualitative, build a database of descriptive information

- The framework for such a survey has been described

The unit operation approach is well-suited to identifying potential sources of exposures (Ref EPA White Paper)

Table 4. Potential Sources of Occupational Exposure for Various Synthesis Methods (adapted from Aitken, 2004)

Synthesis Process	Particle Formation	Exposure Source or Worker Activity	Primary Exposure Route
Gas Phase	in air	Direct leakage from reactor, especially if the reactor is operated at positive pressure.	Inhalation
		Product recovery from bag filters in reactors.	Inhalation / Dermal
		Processing and packaging of dry powder.	Inhalation / Dermal
		Equipment cleaning/maintenance (including reactor evacuation and spent filters).	Dermal (and Inhalation during reactor evacuation)
Vapor Deposition	on substrate	Product recovery from reactor/dry contamination of workplace.	Inhalation
		Processing and packaging of dry powder.	Inhalation / Dermal
		Equipment cleaning/maintenance (including reactor evacuation).	Dermal (and Inhalation during reactor evacuation)
Colloidal/ Attrition	liquid suspension	If liquid suspension is processed into a powder, potential exposure during spray drying to create a powder, and the processing and packaging of the dry powder.	Inhalation / Dermal
		Equipment cleaning/maintenance.	Dermal

The unit operation approach is well-suited to identifying potential sources of exposures (Ref NIOSH Draft Guidance)

Develop qualitative and quantitative exposure survey protocols

- Can existing public health geographical information systems (GIS) and infrastructure to be used for effective sharing of nanotechnology occupational safety and health data including exposure data?

Probably not
at least under existing paradigms

- These approaches have been used for hazard surveillance in traffic-related studies, at hazardous waste sites, other air and water contamination-related exposures
- Application to nanomaterial exposures raises issues of confidentiality, trade secrets, access, etc…

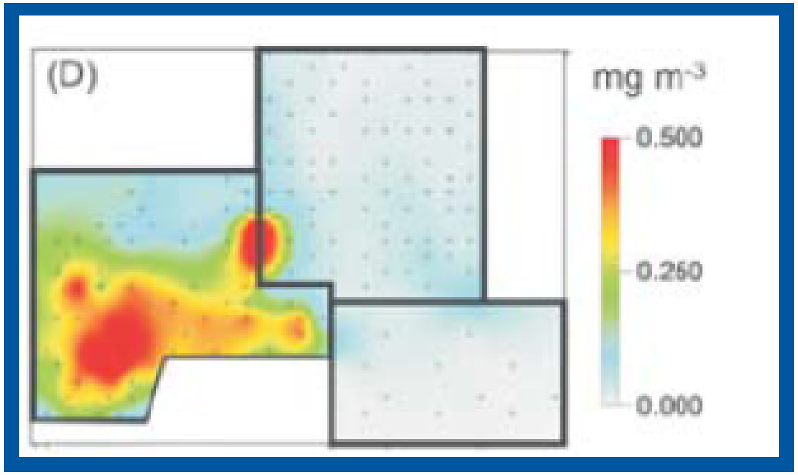
Develop qualitative and quantitative exposure survey protocols

- Can personal exposures be measured?
  - Not yet, …but soon
    - Hierarchy of exposure measures
      - Personal real time
      - Personal averaged
      - Area concentrations representative of personal exposures
      - Categorical exposure classifications
  - Until then:
    - Apply existing measurement technologies
    - Devise strategies to capture the biologically relevant characteristics of exposures

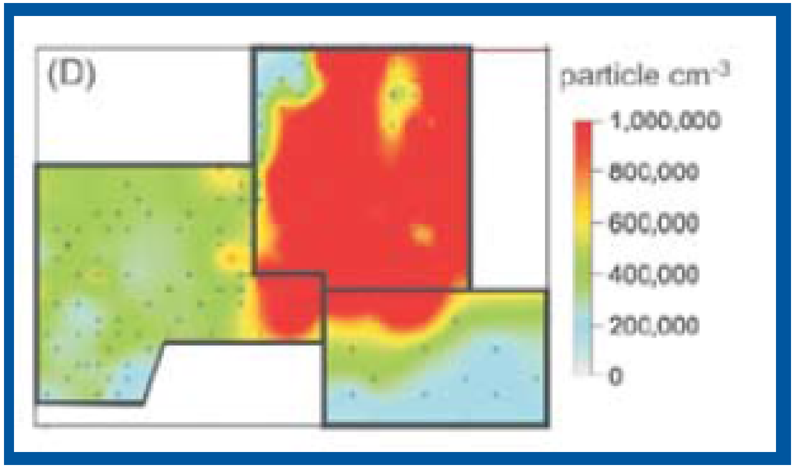
Table 3: Examples of instruments and techniques allowing characterization of NPs aerosols

Parameter	Instruments	Remarks
Mass and granulometric distribution	Cascade impactors	Berner or micro-orifice cascade impactors allow gravimetric analysis of stages finer than 100 nm during individual assessment.
	TEOM	The Tapered Oscillating Element Microbalance (TEOM) preceded by a granulometric selector determines the mass concentration of nanoaerosols.
	ELPI (Electrical Low Pressure Impactor)	The Electrical Low Pressure Impactor (ELPI) allows real-time detection according to size of the active surface concentration and gives a granulometric distribution of the aerosol. If the charge and density of the particles are known or assumed, the data then can be interpreted in terms of mass concentration. The samples at each stage then can be analyzed in the laboratory.
	SMPS (Scanning Mobility Particle Sizer)	Real-time detection according to size of the particle number concentration gives a granulometric distribution of the aerosol. Knowledge of the shape and density of the particles then allows estimating of the mass concentration.
Number and granulometric distribution	CNC	Condensation nucleus counters (CNC) allow particle number concentration measurements in real time within the particle diameter detection limits. Without a granulometric selector, the CNC is not specific to the nanometric field. P-Trak offers screening with an upper limit of 1000 nm. TSI model 3007 is another example.
	SMPS	The Scanning Mobility Particle Sizer (SMPS) allows real-time detection according to the electrical mobility diameter (related to size) of the particle number concentration.
	Electron microscopy	Offline electron microscopic analysis can provide information on granulometric distribution and on the aerosol's particle number concentration.
	ELPI	Real-time detection according to size and active surface concentration gives a granulometric distribution of the aerosol. If the charge and density of the particles are known or assumed, the data then can be interpreted in terms of particle number concentration. The samples at each stage then can be analyzed in the laboratory.
Specific surface area and granulometric distribution	Diffusion chargers	Commercially available diffusion chargers allow real-time measurement of the active surface of the aerosol and have a response in relation to the active surface of particles smaller than 100 nm. These instruments are NP-size specific if they are used with an appropriate pre-separator.
	ELPI	The ELPI allows real-time detection of the aerodynamic diameter according to size and active surface concentration. The samples at each stage can then be analyzed in the laboratory.
	Electron microscopy	Electron microscopic analysis can provide information on the surface of particles in relation to their size. Transmission electron microscopy provides direct information on the projected surface of the particles analyzed, which can be linked to the geometric surface for certain forms of particles.
	SMPS	The SMPS allows real-time detection according to the electrical mobility diameter (related to size) of the particle number concentration. Under certain conditions, the data can be interpreted in terms of specific surface area.
	Parallel use of SMPS and ELPI	The differences in the aerodynamic diameter and electrical mobility measurements can be used to deduce the fractal size of the particles, thus allowing a particle surface estimate.

Number versus mass concentration in machining plant



Mass concentration map



Number concentration map

High mass concentrations do not indicate high number concentrations.

Source: Peters TM, Heitbrink WA, Evans DE, Slavin TJ, Maynard AD [2006]. The mapping of fine and ultrafine particle concentrations in an engine machining and assembly facility. Ann Occup Hyg *50*(3):249–257.

Develop qualitative and quantitative exposure survey protocols

- Are there adequate emission measurement protocols? What are the limitations?
- How can emission measurements be translated to personal exposures?

Draft protocols from NIOSH (Approaches to Safe Nanotechnology)

- Identify potential sources of emissions
- Conduct particle concentration sampling
  - Background measurements
  - Area sampling
- Conduct filter-based area and personal air sampling

From the EPA Nanotechnology White Paper

- The models used by EPA's Office of Pollution Prevention and Toxics (OPPT) to assess environmental fate and exposure, are, for the most part, designed to provide estimates for organic molecules with defined and discrete structures.
- These models are not designed for use on inorganic materials; therefore, they cannot be applied to inorganic nanomaterials.
- Many models derive their estimates from structural information and require that a precise structure of the material of interest be provided.
- Since many of the nanomaterials in current use, such as quantum dots, ceramics and metals, are solids without discrete molecular structures, it is not possible to provide the precise chemical structures that these models need.

Availability of emission models

- There are a few investigations reporting nanoparticle emission measurements and modeling
- Scenarios include high-speed machining, cooking, laser ablation, and vehicle exhaust

Observations on modeling approaches (EPA Nanotechnology White Paper)

- In general, models used to assess the environmental fate and exposure to chemicals are not applicable to intentionally produced nanomaterials.
- …new models may have to be developed to provide estimations for these materials; however, models cannot be developed without the experimental data needed to design and validate them.
- Before the environmental fate, transport and multimedia partitioning of nanomaterials can be effectively modeled, reliable experimental data must be acquired for a variety of intentionally produced nanomaterials

Current research from the NNI

- **D5-3 *Experimental and Numerical Simulation of the Fate of Airborne Nanoparticles from a Leak in a Manufacturing Process to Assess Worker Exposure***
- **Award #** 0646236 **Agency** NSF
- **Lead Institution** University of Minnesota-Twin Cities **Type**Extramural
- **Explanatory Notes**
- **Abstract**

Explore utility and feasibility of exposure registries

- *Are exposure registries feasible?*
- *What are the limitations?*

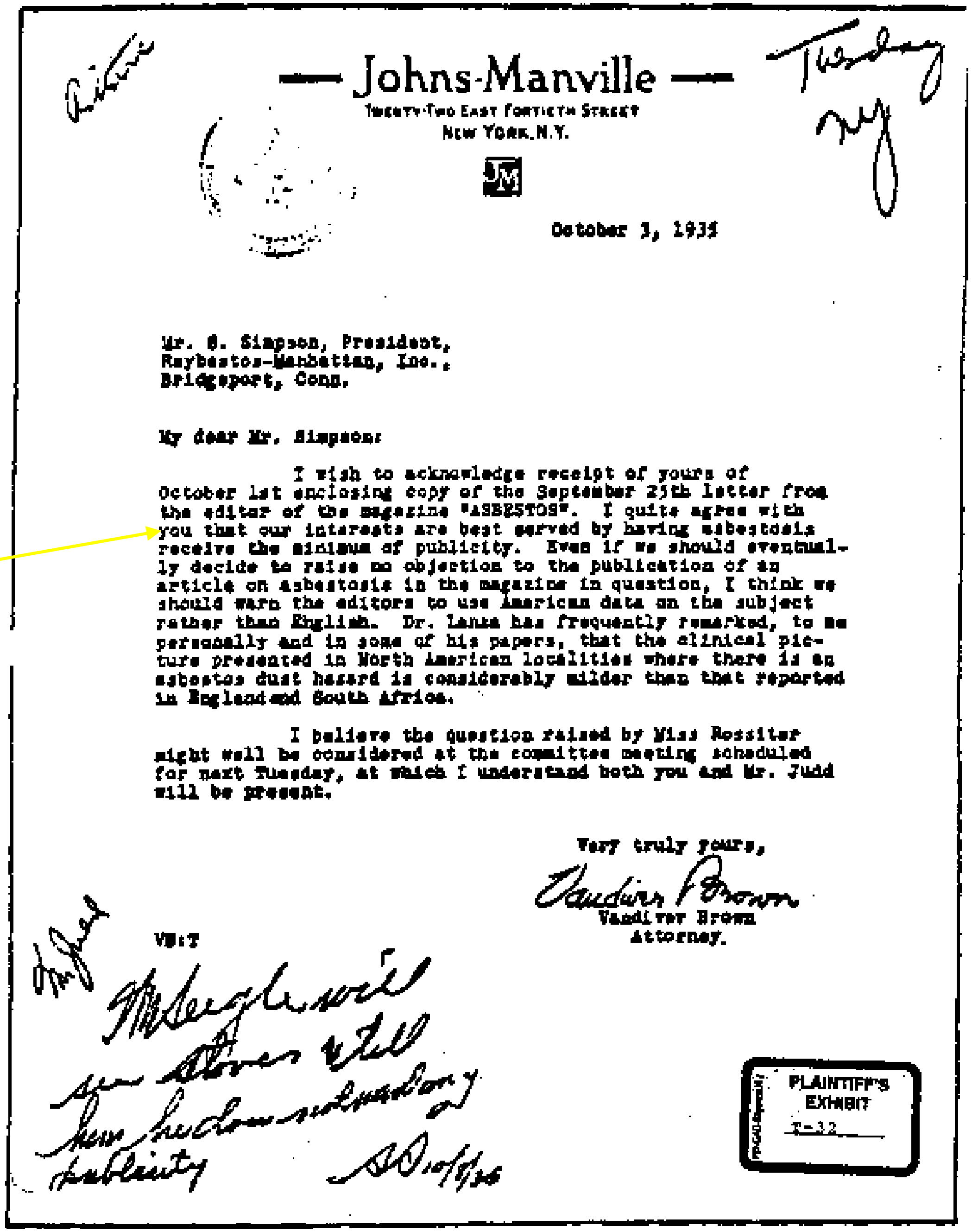
Exposure registries are not only feasible, they are essential

- A National Nanomaterial Exposure Survey would provide the foundation for an exposure registry
- A well-documented registry of workers potentially exposed to nanomaterials would direct research, medical surveillance, and inform risk management and policy decisions

NIOSH Feb 2009

- Hazard surveillance for engineered nanoparticles is an essential component of any occupational health surveillance effort and is used for defining the elements of the risk management program.
- Hazard surveillance should include the identification of work tasks and processes that involve the production and use of engineered nanoparticles, and should be viewed as one of the most critical components of any risk management program.

How different would history be if at this point, Vandiver Brown had said “In the face of these concerns, I believe we should thoroughly document the nature and extent of our employees’ exposures. “



Johns-Manville
Twenty-Two East Fortieth Street
New York, N.Y.

October 3, 1935

Mr. S. Simpson, President,
Raybestos-Manhattan, Inc.,
Bridgeport, Conn.

My dear Mr. Simpson:

I wish to acknowledge receipt of yours of October 1st enclosing copy of the September 25th letter from the editor of the magazine "ASBESTOS". I quite agree with you that our interests are best served by having asbestosis receive the minimum of publicity. Even if we should eventually decide to raise no objection to the publication of an article on asbestosis in the magazine in question, I think we should warn the editors to use American data on the subject rather than English. Dr. Lanza has frequently remarked, to me personally and in some of his papers, that the clinical picture presented in North American localities where there is an asbestos dust hazard is considerably milder than that reported in England and South Africa.

I believe the question raised by Miss Rossiter might well be considered at the committee meeting scheduled for next Tuesday, at which I understand both you and Mr. Judd will be present.

Very truly yours,

Vandiver Brown
Attorney.

VB:T

PLAINTIFF'S EXHIBIT
T-32